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THE FORM OF THE CONDUCTANCE FUNCTION IN DILUTE SOLUTIONS.

BY CHARLES A. KRAUS.

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Some years ago Kraus and Bray¹ showed that in the case of a large number of electrolytic solutions the mass-action law is approached as a limiting case.² In a series of papers which recently appeared in *THIS JOURNAL*, Washburn³ has described a method of extrapolating for Λ_0 which is based on this result. He adds, however, the arbitrary assumption that at high dilutions the function $C\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)$ approaches its limiting value asymptotic to a line parallel to the C -axis. While he does not so state, he nevertheless implies that this method of approach is the only one compatible with the assumption that the mass-action law is a limiting form of a more general function. He applies his method of extrapolation to conductance measurements carried out under his direction by Weiland⁴ and reaches certain conclusions which he believes to be decisive. These conclusions are obviously dependent upon the assump-

¹ *This Journal*, 38, 1325 et seq. (1913).

² They did not discuss in detail the precise manner in which the limiting form is approached, but this may be inferred from their equation.

³ *This Journal*, 40, 728 (1918).

⁴ *ibid.*, 40, 151 (1918).

tions made and it is the purpose of this paper to examine these assumptions in order to determine whether or not the conclusions derived therefrom are valid.

The method which Washburn employs is a graphical one involving two graphs, one between the equivalent conductance and the concentration, the other between the function $CA^2/\Lambda_0(\Lambda_0 - \Lambda)$ and the concentration. In order to make clear what it implies, it will be necessary to examine these two graphs. Let us assume for the moment that we have a binary electrolyte which obeys the mass-action law. We have then

$$\frac{CA^2}{\Lambda_0(\Lambda_0 - \Lambda)} = K, \quad (I)$$

where C is the concentration, Λ is the equivalent conductance, Λ_0 is the limiting value which the conductance approaches as the concentration becomes indefinitely small, and K is the mass-action constant. If we have a very dilute solution of a highly ionized electrolyte, the ratio Λ/Λ_0 approaches unity. In any case its variation becomes negligible in comparison with the difference $\Lambda_0 - \Lambda$. If we introduce this simplifying condition in Equation I, we have

$$\frac{CA}{\Lambda_0 - \Lambda} = K, \quad (II)$$

or

$$CA = K\Lambda_0 - K\Lambda. \quad (III)$$

From Equation III we have

$$d\Lambda/d(CA) = -1/K, \quad (IV) \quad d^2\Lambda/d(CA)^2 = 0. \quad (V)$$

This means that, if we plot values Λ against those of CA for a dilute solution, the graph begins on the axis of Λ at the value Λ_0 and proceeds downward toward the axis of CA as a straight line, the slope being given by the constant value $-1/K$, from which it follows that K is equal to the cotangent of the acute angle which the line makes with the Λ -axis. If we employ the concentration C in the place of the specific conductance CA , the graph will have the same form since Λ increases only very slowly in comparison with $\Lambda_0 - \Lambda$ and C . The slope will then be given by the expression $-\Lambda_0/K$.¹ What has been said with regard to the curve connecting CA and Λ holds equally for a curve between C and Λ so long as the concentration is sufficiently low.

The mass-action law does not hold in the case of strong electrolyte. The function

¹ In the general case we have $d\Lambda/d(CA) = -\Lambda^2/K\Lambda_0^2$, and $d\Lambda/dC = -\Lambda^2/K(\alpha\Lambda_0^2 + \Lambda_0\Lambda)$. It is obvious that as Λ approaches the value Λ_0 , the expressions for the differential coefficient approach the limiting values $-1/K$ and $-\Lambda_0/K$ respectively. If the ionization of an electrolyte were 99%, neglecting the difference between the values Λ_0 and Λ in comparison with Λ_0 would scarcely cause an appreciable error in the notion of the tangent.

$$\frac{CA^2}{A_0(A_0 - \Lambda)} = K' \quad (\text{VI})$$

increases with increasing concentration. If we plot values of C or CA along the x -axis, and values of Λ along the y -axis, the slope of the curve at any point is given by the equation

$$d\Lambda/d(C\Lambda) = -1/K' \quad (\text{VII})$$

Since K' increases with increasing concentration, it follows that the slope decreases with increasing concentration, *i. e.*, the curve bends away from the axis of C , or is convex toward this axis. This follows also from the sign of the second differential coefficient. We have

$$\frac{d^2\Lambda}{d(C\Lambda)^2} = \frac{1}{dK'/d(C\Lambda)} \quad (\text{VIII})$$

The second differential coefficient is positive, since, according to experiment $dK'/d(C\Lambda)$ is always positive. But this is the condition that the curve shall be convex toward the axis of CA . The continuous curve in Fig. 5 is of this type.¹ Generally the curve will have its greatest curvature at that point for which $dK'/d(C\Lambda)$ is greatest, that is, at that point where K' changes most rapidly.

Having established the geometrical properties of the curve in which C (or CA) and Λ are plotted as variables, let us examine the curve obtained when $K' = CA^2/A_0(A_0 - \Lambda)$ and C (or CA) are plotted as variables. Let us assume the general function

$$K' = \frac{CA^2}{A_0(A_0 - \Lambda)} = F(CA) \text{ or } F(C), \quad (\text{IX})$$

assuming the solutions to be dilute. $F(C)$ is a purely empirical function whose nature can be obtained from a graph between K' and C . Let us assume values of C to be plotted as abscissas. We have then

$$dK'/dC = F'(C), \quad (\text{X})$$

and

$$d^2K'/dC^2 = F''(C). \quad (\text{XI})$$

Since, according to experience, K' increases with increasing concentration, it follows that $dK'/dC > 0$, *i. e.*, the curve rises as the concentration increases. As regards the second differential coefficient, we know that the curve is concave toward the axis of C up to 10^{-4} *N*. It follows therefore, that throughout this region

¹ From the geometrical relations it follows that $d\Lambda/d(C\Lambda) = \tan \theta$, where θ is the angle which the line from A_0 to the tangent point on the curve makes with the CA -axis. Therefore, we have $K' = \cot \phi$ where ϕ is the angle which the line makes with the Λ -axis. This is evident from Fig. 4.

$$\frac{d^2K'}{dC^2} < 0. \quad (\text{XII})$$

If this curvature continues to be maintained at lower concentrations than $10^{-4} N$ down to any desired value, then it follows that the tangent to the curve as it cuts the axis of K' makes with the C, Λ -axis an angle greater than zero. In other words, such a curve will not become asymptotic to a line parallel to the C -axis. Algebraically this is expressed by the equation

$$\lim_{C \rightarrow 0} \frac{dK'}{dC} > 0. \quad (\text{XIII})$$

Whether or not the function, IX, will ultimately suffer a reversal in the sign of curvature, cannot be determined on *a priori* grounds. We may, however, examine the function $F(C)$ and determine how its form changes in the regions accessible to experiment, whether or not, for example, d^2K'/dC^2 increases or decreases as the concentration decreases. If it is found that the curvature increases with decreasing concentration down to $10^{-4} N$, then, from our general notions as to the nature of dilute solutions, we should have reasonable grounds for assuming that the curvature continues to increase at lower concentrations. Certainly we should not be justified in assuming that the sign of curvature changes over a very short interval of concentration change.

Kraus and Bray examined practically all the available data on non-aqueous solutions, and found that the relation between conductance and concentration is expressed within the limits of experimental error by the equation

$$K' = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} = \frac{D(C\Lambda)^m}{\Lambda_0^m} + K, \quad (\text{XIV})$$

where, as before, Λ_0 is the limiting value which the equivalent conductance approaches as the concentration diminishes without limit, while K is a limiting value which K' approaches under the same conditions. The constants D and m have no physical significance, but are both positive, while m has been found always less than 2. The above equation was found to fit the experimental values in the case of non-aqueous solutions within the limits of experimental error from the greatest dilutions to concentrations, in some instances, greater than normal. In the case of aqueous solutions there is some question as to the applicability of this function. Nevertheless, since this function reproduces the experimental values fairly closely from 3.0 to 0.001 N , we may assume that it holds approximately. In any case, it is a reasonable procedure to assume some function, which fits experimental values fairly closely over a considerable range of concentration, and then to investigate the changes which the constants undergo as we proceed along the curve.

Let us examine, then, the conductance function XIV. Applying Equations X and XI and using CA as variable in place of C^1 , we have

$$\frac{dK'}{d(CA)} = \frac{Dm(CA)^{m-1}}{\Lambda_0^m}, \quad (XV)$$

and

$$\frac{d^2K'}{d(CA)^2} = \frac{Dm(m-1)(CA)^{m-2}}{\Lambda_0^m}, \quad (XVI)$$

respectively.

Equation XV shows that the curve has a positive tangent, *i. e.*, with increasing values of CA , K' increases. The curvature is determined by Equation XVI, which shows that this is determined by the value of the constant m . When we have $m < 1$, then

$$\frac{d^2K'}{d(CA)^2} < 0, \quad (XVII)$$

while when $m > 1$

$$\frac{d^2K'}{d(CA)^2} > 0, \quad (XVIII)$$

and when $m = 1$

$$\frac{d^2K'}{d(CA)^2} = 0. \quad (XIX)$$

It follows therefore that, for values of $m < 1$, the curve of K' and CA is concave toward the axis of CA , and, for $m > 1$, it is convex toward this axis. When $m = 1$, we have a limiting case, the curve has zero curvature, *i. e.*, K' increases as a linear function of CA .

From Equation XV we see also that for $m < 1$

$$\lim_{C \rightarrow 0} \frac{dK'}{d(CA)} = \infty, \quad (XX)$$

while for $m > 1$

$$\lim_{C \rightarrow 0} \frac{dK'}{d(CA)} = 0. \quad (XXI)$$

That is, in the case of an electrolytic solution for which m is less than unity, the function K' approaches the limiting value K asymptotic to the axis of K' , while for one in which $m > 1$, K' approaches the value K tangent to a line passing through K parallel to the CA -axis. In the limiting case $m = 1$, K' approaches K along the line whose tangent is Dm/Λ_0^m .

Whether m is greater or less than unity, the curvature increases as the

¹ In dilute solutions either C or CA may be employed as desired. If we use Equation XIV, however, CA is preferably used as variable, since in this case the result is not restricted to dilute solutions.

concentration decreases.¹ This is particularly apparent for values of m differing greatly from unity, as in the case of aqueous solutions. When m is nearly unity, the curve differs only a little from a straight line. The general form of the curves will be apparent from Fig. 1, where Curve I is calculated for the constants: $m = 0.52$, $D = 1.703$, $K = 0.001$ and $A_0 = 129.9$. This curve corresponds to that of potassium chloride

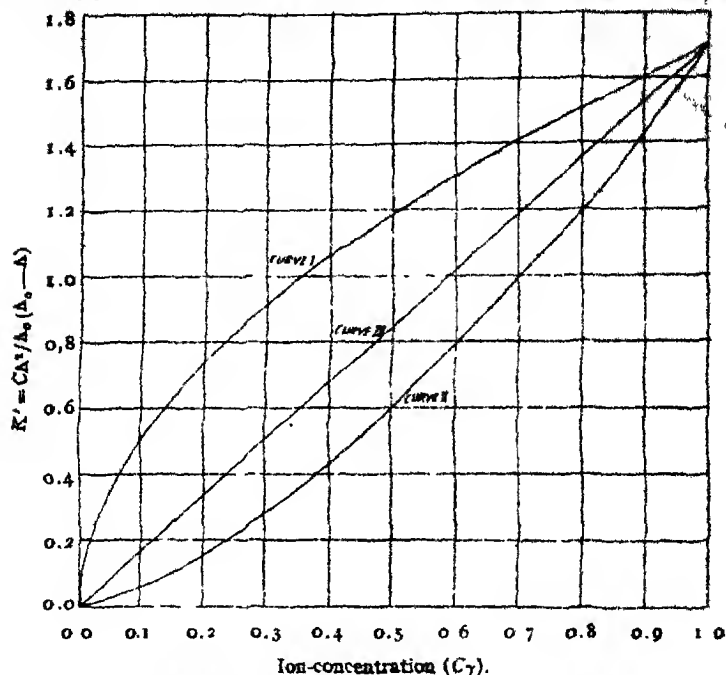


Fig. 1—Showing typical K' -curves for different values of m .

¹ For the radius of curvature we have the expression

$$R = \frac{\left[1 + \frac{dK'}{d(CA)}\right]^{3/2}}{\frac{d^2K'}{d(CA)^2}}, \quad \text{or} \quad R^{1/2} = \frac{(CA)^{\frac{2(2-m)}{3}}}{[Dm(m-1)]^{1/2}} + \frac{m^{1/2}D^{1/2}(CA)^{\frac{2(2-m)}{3}}}{(m-1)^{1/2}}.$$

The coefficient $2-m$ of the exponent of the first term of the right-hand member of the equation is positive for all values of m less than 2. Since no case is known of an electrolyte for which m is greater than 2, we need consider only such cases for which $m < 2$. Under these conditions the radius of curvature increases with increasing values of CA so far as the first term is concerned. For $m > 1$, the coefficient $2m-1$ of the exponent of the second term is greater than unity and the radius of curvature increases with increasing values of CA . For $m < 1$, we always have $2-m > 2m-1$ so long as m is not negative. In this case, therefore, the first term overbalances the second and the radius of curvature increases with increasing values of CA . The curvature, therefore, decreases with increasing values of CA for all values of m between 0 and 2.

in water. Curve II is calculated for the same values of the constants except that $m = 1.50$, while Curve III represents the case when $m = 1$. All these curves necessarily pass through the common points $K' = K$, at $CA = 0$, and $K' = D/\Lambda_0^m + K$, at $CA = 1$.

Having determined the geometrical properties of the two graphs with which we have to deal, let us examine Washburn's "New Graphical Method of Extrapolating." After discussing the various methods previously employed in determining Λ_0 , Washburn introduces his method as follows: "In order to avoid the errors involved in what may be called the 'arbitrary function' methods of extrapolating, and also to avoid similar uncertainties involved in attempting a direct graphical extrapolation, the following method has been devised: It seems to the writer that no valid objection¹ can be urged against it. It rests only upon the following two assumptions: (1) That as C decreases, the value of the mass-action expression K_E ² also decreases and will eventually gradually approach a constant, K_0 , at extreme dilutions; and (2) that whatever be the true form of the curve connecting K_E with C , it must be one which does not show deviations from the mass-action law which *increase with dilution*, that is, in dilute solutions the curve must not exhibit any erratic behavior such as a sudden rise or a sudden fall with decreasing concentration." . . . "In other words, it is assumed that those influences which cause a strong electrolyte to deviate from the mass-action law at higher concentrations *gradually and steadily* become smaller and smaller and finally disappear at infinite dilution. No assumption is made as to the actual path over which the values of K_E shall approach the constant limiting value, nor in fact is any assumption whatever made as to the mathematical form of the function which connects the conductivity with the concentration *over any part of the concentration range open to direct measurement*."

The following footnote also appears as noted above: "Unless indeed the assumption that, $\lim_{C \rightarrow 0} dK_E/dC = 0$ is considered an objection."

In practice Washburn applies his method as follows: The measured values of Λ are plotted as ordinates against the measured values of C , or CA as abscissas. Through these points a smooth curve is drawn and values of Λ are interpolated at round concentrations. With these interpolated values of Λ , values of $K' = CA^3/\Lambda_0(\Lambda_0 - \Lambda)$ are calculated for different values of Λ_0 . These values of K' are then plotted against values of C . Four types of curves result, depending on the value of Λ_0 employed in calculating K' . First, for the smaller values of Λ_0 , a curve which at higher concentration is concave toward the axis of C but which,

¹ Author's footnote quoted in text below.

² Washburn's function K_E corresponds to the function K' as employed in this paper, and his constant K_0 corresponds to the constant K .

between a concentration of 2×10^{-4} and $10^{-4} N$, passes through a point of inflexion, after which it is convex toward the axis of concentration, passing through a minimum, and thereafter rising very steeply as the concentration decreases. Second, for larger values of Λ_0 , a curve which is initially concave toward the C -axis, and which passes through two inflexion points at concentrations below $2 \times 10^{-4} N$. Third, for an intermediate value of Λ_0 , a curve concave toward the C -axis, at higher concentrations, which passes through an inflexion point between 2×10^{-4} and $10^{-4} N$, continuing to lower concentrations convex toward the C -axis, finally cutting the axis of K' tangent to a line parallel to the C -axis. Finally, for considerably larger values of Λ_0 , a curve which is everywhere concave toward the C -axis. That value of Λ_0 which gives the third type of curve, Washburn assumes as the correct one.

On examination, it will be found that this method of extrapolation fails to conform to the second assumption made. An "erratic behavior" is to be judged not alone in discontinuities or sudden changes in the value of the primitive function, but also in any unusual changes in its derivatives. If we apply Condition XI with regard to the second differential coefficient, we find thus remarkable behavior: At higher concentration, and down to approximately $2 \times 10^{-4} N$, the curve is concave

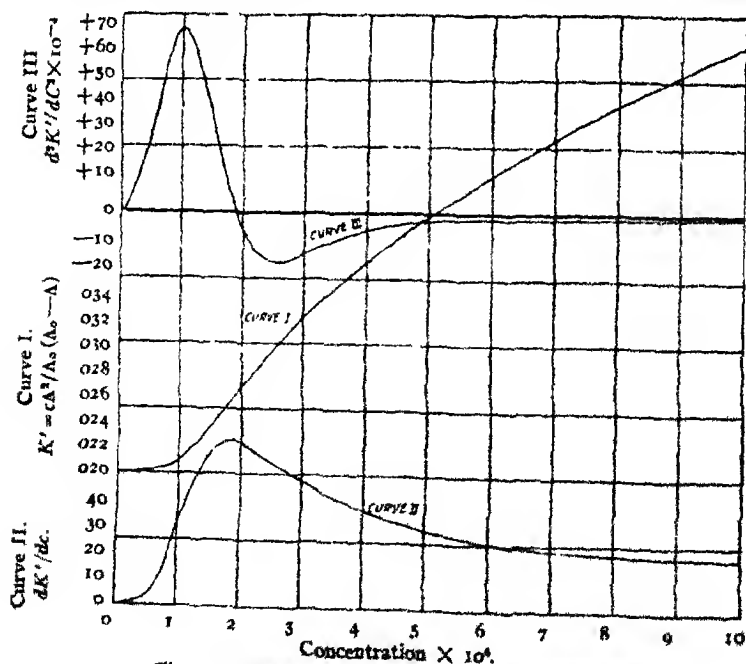


Fig. 2.—Showing derivatives of Washburn's function,

toward the axis of C , the curvature increasing as the concentration decreases. Then the curvature begins to decrease. When a concentration of approximately 10^{-4} has been reached, the curvature passes through zero and thereafter increases with extreme rapidity reaching a maximum a little below $10^{-4} N$ and thereafter again decreasing and approaching zero at zero concentration. In short, in dilute solutions, where we have least reason to expect an erratic behavior of the conductance function, Washburn assumes a function which exhibits extreme complexity. On the other hand, the curve which results from considerably larger values of Λ_0 , is in every way a regular curve which retains, in dilute solution, the same form which it has in concentrated solution and whose curvature increases regularly, with decreasing concentration. The courses of the first and second derivatives of Washburn's function are shown in Fig. 2 as Curves II and III, respectively, while the primitive function is shown as Curve I. Curve I is the reciprocal of the derivative $d\Lambda/dC$ of the graph represented by the broken line in Fig. 5. If the primitive function at low concentrations possesses the same form as at higher concentrations, it has the form of Curve I in Fig. 3,¹ where Curves II and III represent the courses

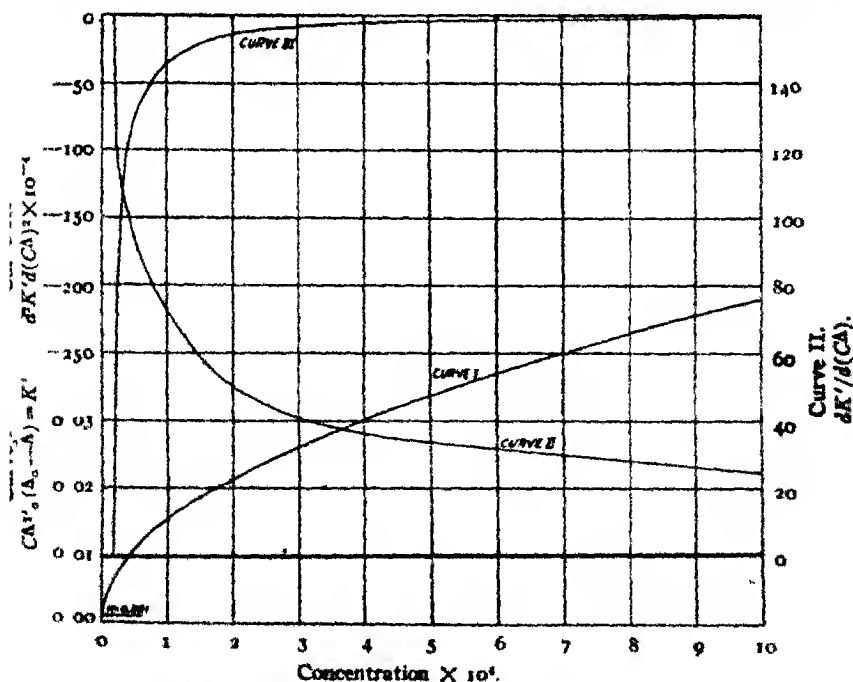


Fig. 3.—Showing derivatives of equation XIV.

¹ In this case CA is employed as variable instead of C , in which case we are not restricted to the condition $\Lambda/\Lambda_0 = 1$. In any case, however, this ratio varies so little

of the first and second derivatives, respectively, of the primitive shown in Curve I.

Washburn's first assumption, also, is not fulfilled by his method of extrapolation for he imposes the condition $\lim_{C \rightarrow 0} dK'/dC = 0$. This condition, it is true, is compatible with the assumption in question, but it is not a necessary condition. The curve of K' , so far as the assumption goes, might intersect the axis of K' not alone at the angle 0° , with the CA -axis, but at any angle from 0° to 90° .

In Fig. 4, the crosses represent experimentally determined values of Λ and of CA , values of Λ being plotted as ordinates and of CA as abscissas. The points in question are those determined by Weiland in his first 3 series of measurements. The points are numbered in order except that the first point of the second series has been omitted. The point marked "K" is due to Kohlrausch and Maltby. Among the points a smooth curve has been drawn as represented by the continuous curve. From the point P , which is in the neighborhood of the last experimental points, let us draw a tangent to the curve and extend it until it cuts the axis of Λ at the value $\Lambda'_0 = 129.74$. If we calculate the value of K' for different points assuming for Λ_0 the value Λ'_0 , we obtain for all points lying on the tangent the value K'_P corresponding to that of the point P . If, on the other hand, a point lies above the tangent, the value of K' calculated will be greater than K'_P , while if it lies below the tangent the corresponding value of K' will be less than K'_P , assuming the same value of Λ_0 to be used in all cases. If, then, assuming $\Lambda_0 = 129.74$, we calculate K' for points along the smooth curve, the value of K' will decrease with decreasing concentration approaching the value K'_P as a limit. In a graph of K' and C , the curve becomes tangent to a line parallel to the C -axis which intersects the K' axis at the value K_P . The concentration at which tangency occurs is C_P corresponding with that of the point P . If a value of Λ_0 is assumed, smaller than Λ'_0 , such as $\Lambda_{01} = 129.64$, for example, the values of K' calculated on this assumption for points on the smooth curve will everywhere be greater than those calculated for a larger value of Λ_0 . The K' , C -curve in this case passes through a minimum corresponding to the point P_1 , at which a line drawn from Λ_{01} to the smooth curve is tangent to that curve. At the point in question, the value of K' will be K'_{P_1} . For a value of Λ_0 greater than $\Lambda'_0 = 129.74$, the K' , C -curve everywhere lies below that calculated on the basis of the latter value. This curve does not pass through a minimum but has two inflexion points. For sufficiently large values of Λ_0 , however, the inflexion points disappear and the K' , C -curve continues everywhere concave to the C -axis without any singularities until it be-
in comparison with C that the form of the curves is not affected materially. The constants of Curve I are those for potassium chloride whose values are given below.

comes tangent to the K' axis at some definite value K . In Fig. 4, the value $\Lambda_0 = 129.9$, at which the smooth curve, extended (shown by the broken line), cuts the Λ -axis, is such that the corresponding K' , C -curve becomes tangent to the K' axis at the value $K = 0.001$. This value is equal to the cotangent of the angle, shown in the figure, at which the Λ , C -curve cuts the Λ -axis.

If, in drawing the smooth curve, the last points, 1, 6 and 10, had been neglected, the curve might have been halted at the point P_1 , and extended to cut the Λ -axis at the value $\Lambda_{01} = 129.64$. In this case a K' , C -curve would have been obtained which approached the limiting value K'_P , as determined by the cotangent of the angle which the tangent $\Lambda_{01}P_1$ makes with the Λ -axis. If the points at lower concentrations were lacking up to P_1 , for example, a value $\Lambda_{02} = 129.44$ could be extrapolated, and the values of K' calculated on the basis of this value of Λ_0 would approach a limiting value K'_P , determined by the cotangent of the angle as shown in the figure.

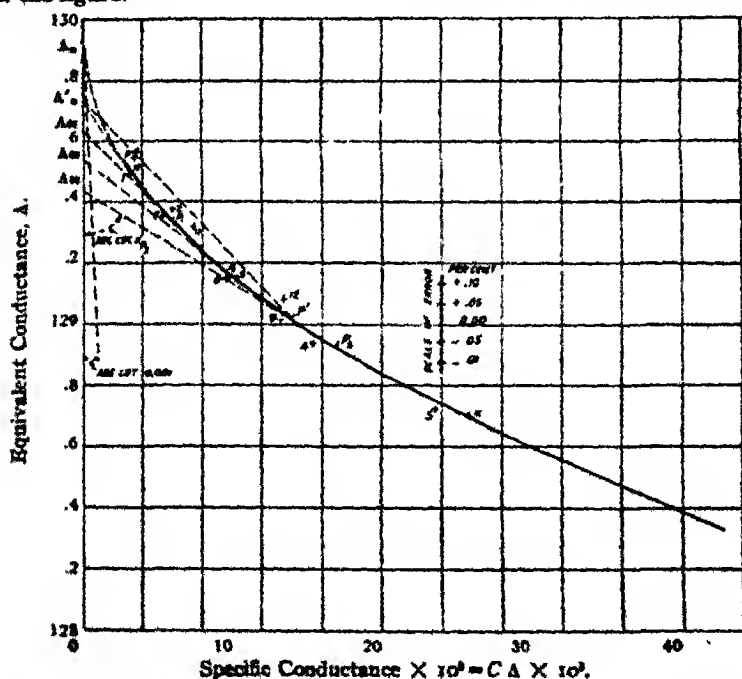


Fig. 4.—Illustrating method of extrapolating for Λ_0 .

So long as the points at the lower concentrations are available, it is clear that the tangents drawn to P_2 and P_3 are out of the question. On the other hand, the tangent to P_1 lies within the limits of experimental error of two of the three points near P . The tangents drawn to P_2 and

to P_1 differ by less than 0.02% at the lowest concentration at which measurements have been made. The values of Λ_0 based on these two tangents are 129.74 and 129.64 respectively. If we grant for the moment that the method of extrapolation here in question is correct, it is evident that the values obtained for Λ_0 and K admit of considerable variation within the limits of experimental error. But there is no reason for believing that this method of extrapolation is justified. In fact, as we have seen, this method of extrapolation imposes on the conductance function a degree of complexity which appears altogether improbable. If we assume that the conductance function in dilute solutions follows the same general trend as it does in concentrated solutions,¹ no singularities arise either in the function itself or in its first and second derivatives. The extrapolation of this function is indicated in Fig. 4 by the continuation of the curve as a broken line until it intersects the Λ -axis at the value 129.9. From the equation of the curve, which is given below, it follows that the limiting angle at which the curve approaches the axis is $\text{arc cot } K = 0.001$. Here again we have another value of Λ_0 consistent with the experimental points well within the limits of error. An examination of Fig. 4 will make it clear that the values of Λ_0 and of K are not to be determined with any degree of precision from measurements in dilute solutions alone. Even higher values than 129.9 would be in agreement with the experimental points within the limits of error. To extrapolate the function we must take into account the experimental values at higher concentrations.

The foregoing analysis shows that Washburn's method of extrapolation by means of the K' , C -plot must give identical values of Λ_0 with those obtained from the Λ , C -plot if, from the last point on the experimental curve, a straight line is drawn tangent to this curve until it intersects the Λ -axis. The statement, "No assumption is made as to the actual path over which values of K_g shall approach the constant limiting value" is not correct. This method of extrapolation is based on the assumption that K' approaches its limiting value horizontally.

Let us now examine the conclusions which Weiland draws from his experiments. He made 5 series of determinations between approximately 10^{-4} and 2×10^{-3} N ; two of the series comprise 4 points, two others 3 points, and the fifth comprises 4 points up to 1.5×10^{-4} N . Weiland states that in the most dilute solutions the error may reach 0.05%, due to error in weighing out the salt. If this is true, some of the more concentrated solutions may be in error to this extent, since they were made up by weighing out successive amounts of salt of this order of magnitude.

¹ It may safely be assumed that the C , Λ -curve is not concave toward the C -axis at any point for, otherwise, the value of K' would diminish with increasing concentration. There is no experimental evidence which indicates such a course.

Weiland ascribes the failure of the points of different series to lie on the same smooth curve to variations in the cell constant. In 3 runs, however, he measured solutions whose concentration lay near $10^{-3} N$. As may be seen from Curve A of Weiland's Fig. 10, these determinations check with one another and with those of Kohlrausch within the limits of the electrical measurements. It must be assumed, therefore, that the cell constant did not vary and that any variation of the points from a smooth curve is due to other sources of error. The procedure which Weiland adopts, of treating each series by itself on the assumption that the variations between series are due to changes of the cell constant, does not appear justified, although the rejection of the last series may be allowable on the grounds that some consistent unknown source of error affects it.

Weiland plots the values of Λ as ordinates against those of C as abscissas and draws curves among the points of each series individually. Between 10^{-4} and $2 \times 10^{-3} N$ these curves approximate closely to straight lines, particularly in the more dilute solutions. These curves probably lie within the limits of experimental error. Nevertheless, in drawing the curves so as to approximate straight lines, a tacit assumption is made as to the manner in which the curves should proceed, and since Weiland's conclusions rest entirely upon the form of the curve in these dilute solutions, his conclusions are a result of this assumption. On the smooth curves, Weiland interpolates values at 10^{-4} , 7.5×10^{-5} , 5×10^{-5} and $2 \times 10^{-5} N$. With these interpolated values he then calculates the values of K' for different assumed values of Λ_0 and plots them against the concentration. That value of Λ_0 , which causes the curve to approach the axis of K' parallel to the axis of C , he assumes as the correct one,¹ and the intercept on the K' -axis he assumes as the value of the mass-action constant K .

As was shown above, any curve in the C, Λ -plot which is extrapolated as a straight line will give a value of Λ_0 yielding a corresponding K', C -graph which approaches the K' -axis parallel to the C -axis and which intersects the K' -axis giving a value of the mass-action constant in harmony with this value of Λ_0 . The fact that a certain value of Λ_0 renders the K', C -curve horizontal and yields a corresponding intercept on the

¹ Washburn (*Loc. cit.*, p. 130) believes that, since a change of 0.01 unit in the value of Λ_0 causes the K', C -curve to rise or fall rapidly, the value of Λ_0 is determined with approximately this precision and that this precision is greater than it would have been for a direct extrapolation on the C, Λ -plot. It is obvious that if the ends of the curves in the C, Λ -plots had been extrapolated to the concentration zero, the value of Λ_0 would have been determined with the same precision as in the K', C -plot. In both cases the precision is not one of experimental measurements, but of reading off and extrapolating graphs, which is solely a function of the scale used in plotting.

K' -axis, in no wise proves that this is the correct value of Λ_0 , nor that the value of K is the true one, nor, indeed that the mass-action law is obeyed at all, unless the curve drawn in the C, Λ -plot is the only curve which can be drawn through the experimental points which lies within the limits of experimental error and unless this curve is a straight line in the regions where the conductance has been experimentally determined. So long as the points as actually measured lie on a curve in the C, Λ -plot, the mass-action law can not be obeyed and the extrapolation of the curve to zero concentration remains uncertain. In fact, an extrapolation to zero concentration by Washburn's method cannot give a correct result unless the curve in the experimental region is a straight line in the C, Λ -plot.

An inspection of Weiland's Fig. 10, or Figs 4 and 5, of this paper, makes it clear that the limits of error between 10^{-4} and $2 \times 10^{-3} N$ are sufficiently large to make it possible to pass a great many curves among these points, all lying well within the limits of experimental error. Indeed, it will be observed from Weiland's Fig. 10 that 3 series of measurements give points which lie on curves decidedly convex toward the axis of C , while 4 out of 5 points of another series lie on a curve convex in the same direction. Only in the case of one curve, comprizing 3 measurements, do the points lie on a straight line. On the other hand, in not a single case do the points lie on a curve concave toward the C -axis. In the light of these facts, it is difficult to avoid the conclusion that the true form followed by the curve in the C, Λ plot is one convex toward the C -axis and not a straight line as Weiland and Washburn tacitly assume.

Because of the small value of the non-ionized fraction of the salt in these solutions, and the consequent great variation in the function K' due to a small error in the determination of Λ , the true variation of this function with concentration is entirely masked. There is little hope that measurements may be carried out at these high dilutions with sufficient precision to enable us to determine what is the true form of the function. To get a notion of this, we must fall back on other considerations, such as an examination of the variation of the function at higher concentrations and the behavior of other solutions. Kraus and Bray have shown that Equation XIV represents the conductance function within the limits of error in the case of a large number of electrolytes dissolved in several different solvents over a large range of concentration, and for others in more concentrated solutions, no data being available at low concentrations. They showed, also that this equation applies very nearly to aqueous solutions from a concentration of $3 N$ to $10^{-3} N$. To apply the equation over this range in aqueous solutions, however, it was necessary to assume a value of Λ_0 not in harmony with the measurements of Kohl-

rausch and Maltby¹ between 10^{-3} and 10^{-4} *N*. Since the measurements of Weiland confirm those of Kohlrausch, it is evident that this assumption is not allowable. However, it is clear that, in any case, the function applies very nearly, and it is possible that at lower concentrations it will apply more exactly. Even though this equation should not apply exactly, it is of interest to examine what variation the constants undergo as the concentration decreases, and it will be reasonably safe to assume that the direction in which the constants change as the concentration decreases will not undergo a reversal of sign at low concentrations and, in particular, that any such change will not take place in a small interval of concentration.

Employing the measured values of Kohlrausch and Maltby and of Weiland, the constants of Equation XIV were calculated from 10^{-4} *N* to the lowest concentrations measured. The following values were obtained: $m = 0.52$, $D = 1.703$, $\Delta_0 = 129.9$ and $K = 0.001$.² The curve

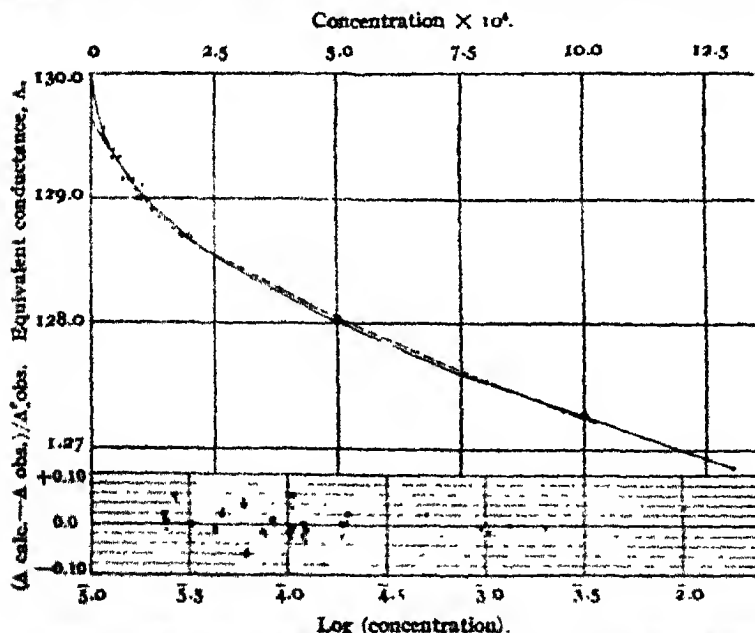


Fig. 5.—Showing deviation of calculated curve from experimental values.

¹ *Wiss. Abh. phys.-tech. Reichsanstalt*, 3, 210 (1900).

² Between 3 *N* and 10^{-3} *N* Kraus and Bray found the values: $m = 0.763$, $D = 2.707$, $\Delta_0 = 128.3$ and $K = 0.080$. On comparison it is evident that D decreases slightly at lower concentrations. The constant K is much smaller than that of Kraus and Bray. Correspondingly the value of Δ_0 is larger. Most significant is the fact that the exponent m is markedly smaller, a result which does not harmonise with the function which Washburn assumes.

of this equation, together with the experimental values,¹ are shown in Fig. 5 up to $10^{-3} N$, values of Λ being plotted as ordinates and those of C as abscissas. At the bottom of the figure are shown the deviations of the experimental values from the calculated curve, up to $10^{-3} N$, the logarithms of the concentrations being plotted as abscissas and the values of the percentage deviations $(\Lambda_{\text{calc.}} - \Lambda_{\text{obs.}})/\Lambda_{\text{obs.}}$ as ordinates. These values are represented by the crosses. The values of Kohlrausch and Maltby are included up to $0.01 N$. The greatest deviation of any point is 0.055% for Weiland's measurement at $6.1994 \times 10^{-4} N$. The curve agrees almost exactly with the mean values of Kohlrausch except at $10^{-3} N$, where the deviation is +0.032% and at $10^{-4} N$ where the deviation is -0.04%. At higher concentrations than $10^{-3} N$, the equation yields values considerably higher than those measured, and the deviation of +0.032% at $10^{-3} N$ is the result of this trend. There can be no question that the function represents the experimental values within the limits of error, up to $10^{-3} N$. The deviation of Weiland's measured values from his best, smooth curves are represented on the same plot by circles.² It will be seen that, even though he had only the dilute solutions to consider, his curve fits the results little if any better than does the calculated curve. The maximum variations from Weiland's smooth curve are slightly greater than those from the equation. Only in the case of the points very near to $10^{-4} N$ does Weiland's curve agree better than that calculated. On the other hand, in the most dilute solutions the experimental values lie slightly more favorable in the case of the calculated curve. At no point, however, is there a constant deviation of the experimental values away from the calculated curve. Wherever the deviations are large, experimental values will be found lying on both sides of the curve. Leaving aside all other considerations, the fact that the experimental values may be so exactly reproduced by means of a function which is so radically different from that which Washburn deduces from the measurements of Weiland in dilute solutions, shows conclusively that Washburn's conclusion as to the mass-action law and the value of Λ_0 are not binding.

When we examine Washburn's conclusion from other points of view it becomes even less probable. Should we grant these conclusions, then, in the light of the geometrical properties of the curve which he obtains,

¹ In this, Weiland's fifth series, which he has himself rejected, is not included.

² Weiland's smooth curve is shown in Fig. 5 as a broken line. It will be observed that it differs from the calculated curve only within the limits of error. It will also be observed that Weiland's curve consists of two parts, one in dilute solutions which approximates a straight line, another in more concentrated solutions which exhibits a slight curvature. The two parts are joined by a short length between 0.9×10^{-4} and $2.5 \times 10^{-4} N$ of very pronounced curvature. The eccentricities of the curve in this region are shown more clearly by the curves in Fig. 2, of which this is the primitive.

FORM OF THE CONDUCTANCE FUNCTION.

the function K' must pass through a series of very rapid changes between 2×10^{-3} and 10^{-4} N . The value of d^2K'/dC^2 must change sign as the curvature of the K' , C -curve, which is increasing in a regular manner with decreasing concentration up to 2.5×10^{-4} N , suddenly begins to decrease, passes through zero, reverses, increases very rapidly and then decreases to zero. Now all these changes take place between 1.5×10^{-4} N and 2.0×10^{-3} N in the case of a function which has been following a regular and simple course up to this point.¹ In view of the fact that the experimental values throughout the region from 2×10^{-3} to 2×10^{-4} N may be reproduced well within the limits of experimental error by the same function which is known to apply at higher concentrations in the case of a very large number of electrolytes, it is evident that the complex function found by Washburn is fictitious and that it is founded on the arbitrary assumption that $\lim_{C \rightarrow 0} dK'/dC = 0$, or, other words, that the K' , C -curve must approach a limiting value asymptotic to a line parallel to the C -axis.

If the K' , C -curve has the form ascribed to it by Washburn, we should expect to find it reproduced in other cases such, for example, as that of the weak acids, which at moderate concentration obey the mass-action law within the limits of experimental error. It develops, however, from the work of Kendall² that this is not the case. If the K' , C -curves are constructed for the acids, they are found to be concave toward the axis of concentration. In terms of Equation XIV, this means that m is less than unity for the acids as it is for strong electrolytes. Kraus and Brice have shown that in non-aqueous solutions m is constant for a given electrolyte in a given solvent over a large range of concentrations. It follows also from their results that there are cases in which the K' , C -curve approaches the K' -axis asymptotic to a line parallel to the C -axis. In such cases, however, the curve has a constant direction of curvature and the curvature increases as the concentration decreases up to the lowest concentrations. Washburn's function, however, does not do this. In the case of this function the curvature is zero at the lowest concentration and changes sign at higher concentrations. The conductance function in the case of different electrolytes in different solvents is remarkably regular. No case is so far on record where the K' , C -curve exhibits an inflexion point if we exclude that which Washburn believes to have discovered.

¹ Inspection of Fig. 2, already described, will make clear the extremely complex character of Washburn's function, while Fig. 3 shows equally clearly the regularity of the function based on the constants given above for Equation XIV. It is to be borne in mind that, at higher concentrations, Washburn's function corresponds to this equation within the limits of experimental error up to 0.01 N .

² *Memoirs of the National Academy of Sciences*, 2, 38 (1913).

As regards the mass-action law, it cannot be said that this law has been shown to be a limiting form of the conductance function in the case of aqueous solutions of strong electrolytes. It is possible that the conductance curve for potassium chloride might be fitted within the limits of error with a value $K = 0$, by slightly reducing the value of m . However, it is equally possible that values of K greater than 0.001 might be employed. In fact, they may be so employed, although they will not reproduce the experimental results quite as closely as the constants given above. Nevertheless, the curves fall within the limit of experimental error. A change of less than 0.05% in a few experimental points might admit a value of K as high as 0.01 or even 0.015. With present experimental material, however, it would be profitless to attempt a solution of this problem.

Finally, it should be borne in mind that the mass-action law is a limiting expression which is approached more or less closely, but which is never fulfilled exactly. As our experiments become more precise, the limits within which it holds constantly recede. The manner in which the limiting form is approached under given conditions depends upon the nature of the solvent and that of the electrolyte while, for a given combination of solvent and electrolyte, it depends upon the temperature. In the case of solutions which exhibit a K' , C -curve concave toward the C -axis, the limiting value is approached asymptotic to the K' -axis.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

A STUDY OF THE HEATS OF DILUTION OF CERTAIN AQUEOUS SALT SOLUTIONS.¹

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A. Introduction.

1. **Purpose of the Investigation.**—A series of investigations² undertaken in this laboratory with the object of studying ionic relationships in aqueous solutions of mixed strong electrolytes has indicated the formation of higher order compounds in the ionization process, in harmony with Werner's ideas in regard to its mechanism.

The method of investigation in the papers referred to has been to study the equilibria between aqueous and metallic solutions, using mixed salt

¹ From a thesis submitted to the Graduate School of the University of Illinois by Allen Edwin Stearn in partial fulfillment of the requirements for the degree of Doctor of Philosophy

² G. MCP Smith, *Am. Chem. J.*, 37, 506 (1907), *THIS JOURNAL*, 32, 502 (1910); 35, 39 (1913); Smith and Ball, *Ibid.*, 39, 179 (1917); Smith and Braley, *Ibid.*, 39, 1545 (1917); 40, 197 (1918); Smith and Rees, *Ibid.*, 40, 1802 (1918).

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solutions and liquid amalgams. The measurement of some colligative property of aqueous solutions seemed to offer a means of testing the ideas from another point of attack, and consequently it was planned: this investigation to measure the reversible molal heats of dilution of certain mixed salt solutions and to compare these with the heats of dilution of solutions of the single salts.

2. *Heats of Dilution.*—The reversible molal heat of dilution, L_D , of an aqueous solution at any concentration is represented by the difference in the heats of vaporization of one mol of water from a solution at that concentration and from pure water.

Thus: $L_D = \bar{L}_s - L_p$.

Here L_D is the reversible molal heat of dilution, \bar{L}_s is the heat of vaporization of one mol of water from the solution in question, and L_p is the heat of vaporization of one mol of water from pure water.

$$\text{But} \quad L = RT^2 \frac{d(\ln p)}{dT}.$$

$$\text{Or} \quad L_D = RT^2 \frac{d \ln p/p_o}{dT}.$$

Without a large mass of experimental data on the partial vapor pressure of water in solutions of various concentrations and at various temperatures, there is no method of calculating the value of L_D without assuming Raoult's law for cases for which we know it does not hold. For dilute solutions where Raoult's law does hold the ratio p/p_o approaches unity so that L_D is zero. In concentrated solutions, however, "or in dilute solutions where the process of dilution is associated with the formation of new molecular complexes, or with the decomposition of those already occurring, the heat of dilution may have a positive or negative value."¹

If, now, one should measure the reversible molal heat of dilution for a given concentration of solutions of single salts, and then for an equivalent concentration of a solution of the mixed salts, one might expect to find the value in the latter case to be somewhere near the sum of the other values unless affected by the formation of new molecular complexes.

B. Materials.

The strontium chloride was in the form of "pure crystals." Most of the material was recrystallized once from water. This procedure in the light of our results seems unnecessary when it is considered that the heat effects in solutions as concentrated as 0.2 *N* are so small as to be hardly measureable. The sodium and potassium chlorides were of various brands, all labeled c. p. These materials are easy to obtain in a state of high purity, and inasmuch as small amounts of impurities have no effect

¹ Kirchhoff, *Pogg. Ann.*, 104, (1856); *Ger. Abh.*, p. 492.

² Nernst, "Theoretical Chemistry," Trans. 6th Ger. Ed., p. 143.

on the results in this work, it was considered unnecessary to purify them further.

C. Apparatus.

The apparatus was a very slight modification of the adiabatic calorimeter of MacInnes and Braham.¹ The instrument itself was that actually employed by Braham, as were the thermometers, Wheatstone bridge, standard cells, etc.

A calorimetric determination of a positive heat effect consisted of measuring the change in resistance of a coil of platinum wire due to the direct dilution of a certain quantity of solution of a certain concentration with a certain quantity of water. Next, a carefully measured quantity of electrical energy was introduced into the solution and the corresponding change in resistance of the same coil measured. For negative heats a slightly different procedure was followed where these heats were comparatively large. In such cases the procedure was to introduce electrical energy into the solution at a carefully measured rate slightly more rapidly than it was taken up in dilution, so that the solution did not cool down below the temperature of the surroundings. The reason for this is that it is much easier to adjust the surroundings to a rising temperature in the calorimeter by means of heating coils, than to a decreasing temperature in the calorimeter where the cooling of the surroundings could not be closely regulated with any degree of satisfaction. After finishing the run as described above, one can calculate the number of calories corresponding to the electrical energy introduced, and the actual number of calories corresponding to the increase in temperature as measured by the change in resistance of the thermometer. The difference is the number of calories due to the heat of dilution. By this procedure the heat capacity of the calorimeter is measured as a part of every determination, and thus inaccuracies due to calculations from questionable data on specific heats of solutions, water equivalent of the calorimeter, slightly varying conditions of the experiments, uncertainties arising from the calibration of the thermometer, etc., are eliminated. Thus by a simple proportion the heat of dilution can be obtained at once. For if H_D is the heat due to dilution, expressed in joules, then

$$H_D : EIT = R_D : R_E,$$

where E is electromotive force, I the current, and T the time in seconds during which the current is passed through the calorimeter heater. R_D and R_E are the changes in temperature, in resistance units, due respectively to the dilution and to the electrical heating.

$$\text{Or} \quad -H_D \text{ (in calories)} : \frac{EIT}{J} = R_D : R_E$$

where J represents Joule's equivalent, 4.184 joules per calorie.

¹ MacInnes and Braham, *THIS JOURNAL*, 39, 2110 (1917)

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Since the relation between the change in resistance and the temperature change is not linear, any large values of R_D or R_E would have to be corrected by means of the relation

$$\Delta t = \frac{100}{(R_{100} - R_0) \left(1 + \frac{d'}{100} - \frac{2d'T}{100^2} \right)} \Delta R$$

in which R_{100} is the resistance of the thermometer in steam at 760 mm pressure, R_0 is its resistance in melting ice, and d' is an empirical constant. MacInnes and Braham determined R_{100} and R_0 for the thermometer employed, and used for d' the value 1.47, recommended by the Bureau of Standards. They found, however, that with the values of R_D and of the magnitude met with in their work, which were even greater than those met with in this investigation, the correction was too small to affect their numerical results in any way; so that if $\Delta R = 0.02395$, then $\Delta t = 0.2395$, just 10 times the numerical value of ΔR .

D. Method.

The salt solutions were made on the basis of gram equivalents of hydrous salt per 1000 g. of water. Their concentration was ascertained by a Volhard determination of the chlorine. The salts used were sodium chloride, potassium chloride and strontium chloride; and the concentrations at which the heats of dilution were determined were 0.2, 0.4, 0.8, 1.6 and 3.2 weight normal.¹ Points on the strontium chloride curve were also obtained for concentrations of 1.2, 2.0, 2.4 and 2.8 wt. *N*. Mixed salt solutions of NaCl : $\frac{1}{2}$ SrCl₂, NaCl : KCl, KCl : $\frac{1}{2}$ SrCl₂, and KC : SrCl₂ were also run at the above mentioned concentrations. These solutions were prepared by diluting a volume of the solution of one of the salts with an equal volume of the solution of the same concentration of the other salt. Thus one volume of 0.8 wt. *N* potassium chloride and one volume of 0.8 wt. *N* sodium chloride were mixed and called 0.8 wt. of the mixed salt.

The value of the reversible molal heat of dilution was obtained by diluting the solution of a definite concentration with decreasing amounts of water, and plotting the heat effects obtained against the number of mols of water added. The curve was found to be a straight line (within the region) so that, by extrapolation to zero mols of water added, the value of the reversible molal heat of dilution at the particular concentration could be obtained.

Accuracy.—The very small values of the heat effects in the case of the more dilute solutions necessitated only approximate results here. MacInnes and Braham state that heat effects of from 50 to 60 calories

¹ Weight normal or wt. *N* is the number of gram equivalents of anhydrous salt per 1000 g. of water.

can be measured with an accuracy of from 4 to 5%.¹ With a total heat effect of from 5 to 20 calories one should not expect much more than 30 to 50% accuracy. In these cases, however, an error of even 100% would change the point on the curve of the concentration plotted against the molal heat effect to such a slight extent that the curve itself would be unaffected. In the case of the larger heat effects, running as high as 600 to 700 calories, the heat change can be measured to within 0.25 to 0.5%, so that the error of the reversible heat value should not be greater than 1 to 2%.

Some justification for the assumption that the molal heat values obtained by diluting a certain quantity of solution with varying amounts of water give a straight line when plotted against the number of mols of

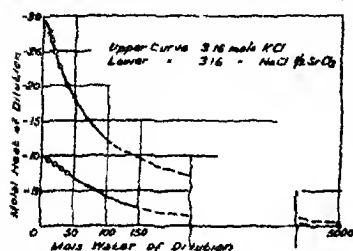


Fig. 1.—Change of molal heat effect with the number of mols of water of dilution over a wide range.

water of dilution is given in Fig. 1. The data for these curves are taken from Tables IV and VII. According to Thomsen² "the value of the thermal change on dilution always varies with variations in the quantity of water of dilution, and this variation, whether positive or negative, seems to have the character of a hyperbolic function of the quantity of water added." As will be seen, the region of the curve on which the

experimental data represented in all the subsequent curves fall is so far from the vertex that the change of slope of the curve has become vanishingly small, and it is practically a straight line. (In Fig. 1, mols of water of dilution per 10,000 g. of solution are plotted as abscissas, and the molal heat effects as ordinates.)

E. Experimental Results.

Tables I to VIII give the data for the heats of dilution of various salt solutions and mixtures. Table I gives in considerable detail the results of a run including resistance readings, results of potentiometer readings, etc. Table I is for the case of a negative heat effect, and a sample calculation from the data included in the table is appended.

In this table, "Time" is the time in seconds during which heat is passed through the calorimeter heater; "Res." is the resistance of the thermometer in ohms; "R" is the change of resistance of the thermometer in ohms multiplied by 10³; "Sol. G." represents the number of grams of solution to be diluted, "Mols H₂O" represents the number of mols of water (assuming 18 g. to the mol) with which the solution was diluted;

¹ It may be stated that to measure the change of resistance due to dilution or to the electrical energy passed into the calorimeter it was *not* necessary to shift a plug in the resistance box.

² Pattison Muir, "Elements of Thermal Chemistry," p. 167.

"Amp" is the current in amperes through the heating coil of the calorimeter; "E. M. F." is the voltage drop across the terminals of this same coil; "Cal" is the number of calories of electrical energy introduced.

The total heat effect of the dilution is given in calories as well as the molal heat effect. The latter value is obtained from the former by dividing it by the number of mols of water of dilution.

A few curves representative of the method of extrapolation are given. Mols of water of dilution are plotted as abscissas and molal heat effects as ordinates. Fig. 2 gives the curve for 2.9 wt. N $SrCl_2$ and that for 0.8 wt. N KCl . The size of the plotted point gives an estimate of the probable accuracy of each point. The radius of the circle represents the variation in the molal heat of dilution due to a variation of 0.00001 ohm in the resistance measurement. In the remainder of the data, the values obtained by drawing similar curves are given but the curves themselves are not included.

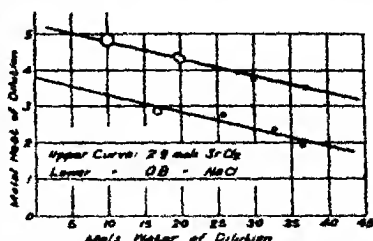


Fig. 2.—Molal heat effect as a function of the amount of water of dilution. (NOTE: Read the ordinates as negative for the $NaCl$ curve.)

Tables III to IX give a condensed summary of some 50 tables of the type of Table I.

TABLE I.—HEAT OF DILUTION OF 3.2 WT. N $NaCl$

Time Sec.	Res. Ohms	$\Delta R \times 10^4$ Ohms	Sol. G.	H_2O Mols.	Current Amp.	E. M. F. Volts	Free energy cal.	Total ht. effect. cal.	Heat effect per mol. cal.
27.41300	1205		10,586	27.4					
100	3875	670			2.322	6.635	1105		
300	5190	1315			2.305	6.58	1090	—546	—19.9
27.43800	2795		10,586	18.45					
100	3605	810			2.335	6.66	1115		
300	4865	1260			2.334	6.66	1115	—398	—21.6
27.44500	2862		10,586	11.22					
300	3808	946			2.33	6.65	1111		
300	5043	1235			2.335	6.66	1115	—238	—22.93*
Reversible Molal Heat of Dilution, L_D									—25.0 cal.

Sample Calculation. If 1115 cal. produce a change in resistance of 1235 units,

then 1111 cal. would produce in the same amount of the same solution a change of resistance of 1231 units. The change measured, however, was only 946 units. A quantity of heat, therefore, equivalent to that represented by a change of resistance of 1231 minus 946 or 285 units was used up by dilution. Therefore if 1235 units are equivalent to 1115 cal., 285 units would be equivalent to 258 cal. This value, then would represent the heat effect due to dilution with 11.22 mols of water. The molal heat effect would then be 258 divided by 11.22, or 22.95 cal. The sign would, of course, be negative.

TABLE II.—HEAT OF DILUTION OF NaCl SOLUTIONS

Concentration. Wt. N.	Solution G.	Water of dilution Mols.	Total heat of dilution cal	Molal heat of dilution cal.	Reversible molal heat of dilution. L_D cal.
3.2	10,586	27.4	—546	—19.9	
		18.45	—398	—21.6	
		11.22	—258	—22.95	—25.0
1.6	8,280	34.83	—245	—7.04	
		22.06	—179	—8.06	
		11.75	—102	—8.67	
0.8	7,986	7.84	—71.1	—9.08	—9.80
		36.45	—70.0	—1.92	
		32.86	—77.8	—2.37	
		25.65	—70.9	—2.76	
0.4	7,900	16.75	—48.44	—2.89	—3.93
		37.72	—29.62	—0.79	
		25.58	—24.09	—0.94	
		21.5	—25.38	—1.18	
		16.5	—21.15	—1.28	
0.2	9,300	12.47	—17.16	—1.38	
		8.86	—12.48	—1.41	—1.60
		28.8	—17.64	—0.61	
		23.4	—17.9	—0.765	
		18.11	—13.4	—0.74	
		14.6	—10.0	—0.69	—0.85

TABLE III.—HEAT OF DILUTION OF KCl SOLUTIONS

Concentration. Wt. N.	Solution. G.	Water of dilution. Mols.	Total heat of dilution cal	Molal heat of dilution cal.	Reversible molal heat of dilution L_D cal.
3.16	8,410	39.0	—781.0	—20.03	
		26.55	—604.3	—22.76	
		19.4	—484.0	—24.94	
		14.4	—382.2	—26.48	
		9.4	—261.2	—27.79	—30.0
1.6	8,000	40.0	—289.5	—7.24	
		30.0	—246.7	—8.22	
		20.0	—177.2	—8.87	
		10.0	—103.3	—10.33	—10.80
0.8	8,000	40.0	—70.68	—1.77	
		30.0	—64.9	—2.16	
		20.0	—48.8	—2.44	
		10.0	—27.8	—2.78	—3.20

TABLE III (continued).

Concentration. Wt. %.	Solution. G.	Water of dilution. Mols.	Total heat of dilution cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. LD cal.
0.4	8,000	34.95	-15.0	-0.43	
		30.0	-13.42	-0.45	
		25.0	-14.1	-0.564	
		20.0	-12.44	-0.622	
		15.0	-10.0	-0.67	-0.95
0.2	7,850	40.0	-2.74	-0.069	
		38.2	-2.92	-0.076	
		34.0	-3.2	-0.094	
		30.0	-3.1	-0.103	
		30.0	-3.25	-0.108	-0.24

TABLE IV.—HEAT OF DILUTION OF SrCl_2 SOLUTIONS.

Concentration. Wt. %.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. LD cal.
3.2	10,000	35.0	189.0	5.4	
		15.0	95.7	6.4	7.2
2.9	9,500	37.2	129.8	3.49	
		30.0	112.4	3.75	
		30.0	114.1	3.80	
		27.7	109.2	3.95	
		20.0	86.33	4.31	
		19.5	85.44	4.38	
		10.0	48.5	4.85	5.40
2.4	10,000	35.0	33.7	0.96	
		25.0	32.5	1.29	2.10
2.0	10,000	35.0	35.5	1.01	
		25.0	31.0	1.23	1.75
1.55	10,000	40.0	23.64	0.59	
		30.0	21.4	0.71	
		30.0	20.92	0.70	
		20.0	17.3	0.86	1.11
1.2	10,000	35.0	18.9	0.54	
		25.0	16.3	0.65	0.90
0.8	10,000	40.0	15.4	0.38	
		30.0	13.0	0.44	
		20.0	10.0	0.50	0.62
0.425	10,000	40.0	11.16	0.28	
		30.0	10.07	0.34	
		20.0	7.4	0.37	0.50
0.2	10,000	40.0	7.88	0.20	
		30.0	6.81	0.23	
		20.0	4.0 ⁺	0.2 ⁺	0.25 ⁺

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TABLE V—HEAT OF DILUTION OF NaCl . KCl SOLUTIONS.

Concentration Wt. %	Solution G	Water of dilution Mols	Total heat of dilution cal	Molal heat of dilution cal	Reversible molal heat of dil. <i>L.D.</i>	
					Obs	Calc.
3.2	10,000	40.0	—780.0	—19.5		
		30.0	—638.0	—21.9		
		20.0	—468.0	—23.4		
		10.0	—256.0	—25.6	—27.8	—20.6
1.6	10,000	40.0	—286.6	—7.16		
		30.0	—230.7	—7.70		
		20.0	—165.1	—8.30		
		10.0	—88.6	—8.86	—9.40	—7.13
0.8	10,000	40.0	—58.54	—1.46		
		30.0	—52.6	—1.75		
		20.0	—39.25	—1.96		
		10.0	—23.8	—2.38	—2.60	—2.53
0.4	10,000	35.0	—21.0	—0.60		
		25.0	—16.0	—0.65		
		15.0	—10.4	—0.70	—0.77	—1.01
0.2*	10,000	40.0	—7.2	—0.18		
		30.0	—5.8	—0.19	—0.2	—0.53

* Another run gave a non measurable result probably due to the fact that equilibrium between the solution and the dilution water had not been reached

TABLE VI—HEAT OF DILUTION OF NaCl $\frac{1}{2}$ SrCl₂ SOLUTIONS

Concentration Wt. %	Solution G	Water of dilution Mols	Total heat of dilution cal	Molal heat of dilution cal	Reversible molal heat of dil. <i>L.D.</i>	
					Obs	Calc.
3.2	10,000	40.0	—303.0	—7.58		
		30.0	—246.6	—8.22		
		20.0	—177.0	—8.85		
		10.0	—95.0	—9.50	—10.20	—8.70
1.6	10,000	40.0	—108.8	—2.72		
		30.0	—93.8	—3.13		
		20.0	—70.2	—3.51		
		10.0	—36.6	—3.65	—4.20	—3.30
0.8	10,000	40.0	—28.2	—0.70		
		30.0	—25.7	—0.86		
		15.0	—16.1	—1.07	—1.30	—1.18
0.4	10,000	40.0	—8.65	—0.22		
		20.0	—6.0	—0.30	—0.40	—0.60
0.2	10,000	40.0	—5.0	—0.12		
		25.0	—3.0	—0.12	—0.1	—0.2

TABLE VII.—HEAT OF DILUTION OF KCl : $1/2$ SrCl₂ SOLUTIONS.

Concentration. Wt. N.	Solution, G.	Water of dilution. Mole.	Total heat of dilution, cal.	Molal heat of dilution, cal.	Reversible molal heat of dil. L.D.	
					Obs.	Calc.
3.2	10,000	40.0	—575.0	—14.37		
		30.0	—472.0	—15.70		
		20.0	—343.5	—17.2		
		10.0	—189.0	—18.9	—20.5	—9.7
(Duplicate Run)						
3.2	10,000	35.0	—514.8	—14.72		
		25.0	—412.0	—16.48		
		15.0	—269.3	—17.95	—20.7	
1.6	10,000	40.0	—168.5	—4.21		
		30.0	—142.0	—4.75		
		20.0	—102.0	—5.10		
		10.0	—54.3	—5.43	—6.0	—2.6
(Duplicate Run)						
1.6	10,000	35.0	—150.5	—4.30		
		25.0	—121.3	—4.86		
		15.0	—77.0	—5.15	—6.0	
0.8	10,000	40.0	—32.4	—0.81		
		30.0	—27.9	—0.93		
		20.0	—20.2	—1.01	—1.22	—0.53

0.4 On four dilutions there was no certain effect measured.

—0.00 —0.00

0.2 Since the 0.4 wt. N solution gave a value which was too small to be measured, no dilutions were made on this solution. The observed value may be safely assumed to be zero. The calculated value is zero.

TABLE VIII.—HEAT OF DILUTION OF KCl : SrCl₂ SOLUTIONS.

Concentration, Wt. N.	Solution, G.	Water of dilution, Mols.	Total heat of dilution, cal.	Molal heat of dilution, cal.	Reversible molal heat of dil. L.D.	
					Obs.	Calc.
3.2	10,000	35.0	—375.0	—10.66		
		25.0	—297.1	—11.88		
		15.0	—184.6	—12.30	—14.0	—3.9
1.6	10,000	35.0	—96.06	—2.75		
		25.0	—86.47	—3.46		
		15.0	—60.80	—4.06	—5.2	—0.6
0.8	10,000	35.0	—18.6	—0.53		
		25.0	—16.5	—0.66		
		15.0	—15.6	—1.04	—1.3	—0.0

F. Discussion.

Figs. 3 to 7 show graphically the change of the reversible molal heat of dilution with the concentration for the various solutions studied. The concentrations expressed in terms of weight normality, are plotted as abscissas; while the heats of dilution in calories per mol of water of dilution, are plotted as ordinates. Fig. 3 shows this for the 3 single salts, by means of curves, plotted to the same scale. Figs. 4 to 7 show the change of the heat of dilution of the various salt mixtures with their con-

centrations. There are 2 curves in each of these 4 figures. The one labeled "Obs." gives the curve as it was observed experimentally, while the one marked "Calc." is plotted from data calculated on the assumption

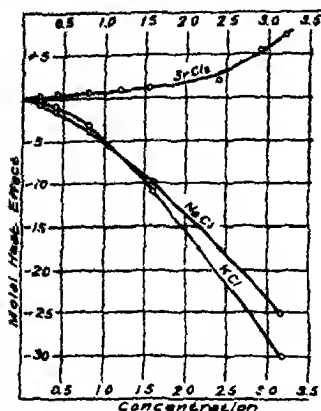


Fig. 3.—Reversible molal heat of dilution as a function of the concentration for solutions of the salts SrCl_2 , NaCl and KCl .

that the heat of dilution of a mixed salt solution is equal to the sum of the heats of dilution of solutions of the various constituents at concentrations equivalent to their concentrations in the mixed solution.

It will be noted at once that, without exception, the observed values lie on a curve which, except at low concentrations, is significantly lower than the curve for the calculated values. This holds even in the case of the mixed sodium and potassium salts where one might expect the least deviation from the calculated values; and is in harmony with the conclusion¹ that the ion-fraction of one of the metallic constituents increases

with increasing total salt concentration, since the two curves, which practically coincide at low concentrations, diverge more and more as the total salt concentration increases. The curve, to be sure, does not indicate which of the ion-fractions increases.

There seems to be no simple relation between the two curves. In the case of the mixture $\text{NaCl} : 1/2 \text{SrCl}_2$ the divergence is even less than in the case of $\text{NaCl} : \text{KCl}$ where the least divergence might be expected. These experimental curves, then, seem to be influenced by 3 factors. There are the specific effects of the two salt components, and there is also the very apparent effect of a third species of molecular aggregate, in all probability a molecular complex of the two salts with varying amounts of water. The concentration of these complexes, in equilibrium with their simple components, will be low at low total salt concentrations, and the specific effect on the curve will be slight in that region so that the two curves should tend to come together at low concentrations. This is, as is observed, the case. As the total salt concentration increases, the concentration of these complexes correspondingly increases and the curve is given a component of slope characteristic of them and depending on two things; namely, their individual "heats of dilution" at the concentration at which they occur, which will depend primarily perhaps on their heats of formation; and the rate of change of their concentration with

¹ Smith and Ball, *THIS JOURNAL*, 39, 179 (1917).

the total salt concentration, or in other words, the value of their equilibrium constant.

Thus, if the value of k in the expression

$$\frac{[(\text{KCl})_x \cdot (\text{NaCl})_y]}{(\text{KCl})^x (\text{NaCl})^y} = k$$

is large, and if the complex $[(\text{KCl})_x \cdot (\text{NaCl})_y]$ has a high heat of dilution we would expect the slope of the experimental curve to be widely divergent from that of the calculated curve, since a substance of high heat

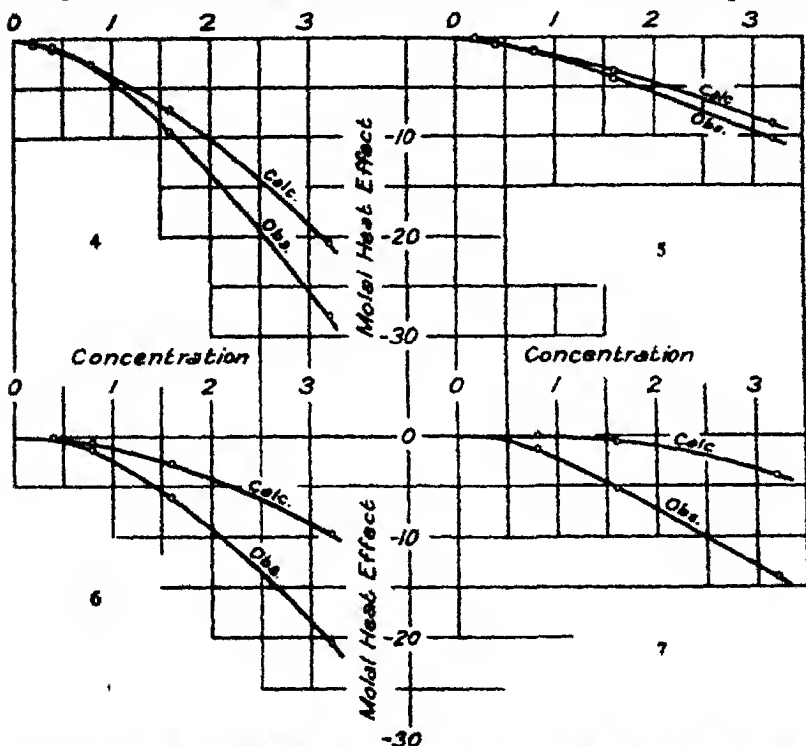


Fig. 4.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution NaCl:KCl.

Fig. 5.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution NaCl:1/2 SrCl₂.

Fig. 6.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution KCl:1/2 SrCl₂.

Fig. 7.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution KCl:SrCl₂.

of dilution is being rapidly produced with increasing total salt concentration. If the value of k is small the curves will diverge less rapidly.

Table IX gives the results of a short series of experiments in which very large quantities of water of dilution, 5.555 mols H₂O and 10,000 g. of

solution, were used. The same tendencies will be noticed as before. In each of the 3 cases of mixed salt solutions the observed value of the molal heat effect is greater (negatively) than the calculated value, a relationship which agrees with those brought out in the curves.

TABLE IX.

Salt.	Conc.	Heat effect.	
		Obs.	Calc.
SrCl ₂ ..	3.2 wt. N	+161
KCl.	3.2 wt. N	-948
NaCl	3.2 wt. N	-1116	..
NaCl : KCl	3.2 wt. N	-1010	-823
NaCl : 1/2 SrCl ₂	3.2 wt. N	-406	-390
KCl : 1/2 SrCl ₂	3.2 wt. N	-542	-350

The assumption of these complexes is not out of harmony with experimental data. The substances $2\text{KCl} \cdot \text{SrCl}_2$ and $2\text{NaCl} \cdot \text{SrCl}_2$ have both been prepared and isolated¹ and ions of the type $(\text{SrCl}_4)^{-}$ and $(\text{BaCl}_4)^{-}$ have been referred to as probably existing in solution.² Indeed it seems probable that there are very few types of compounds which do not tend to form "higher order compounds."³

As was stated in the introduction, according to Nernst the existence of a measurable heat of dilution seems due to the existence of complexes which are formed or decomposed with dilution.⁴

The thermodynamic expression for the reversible molal heat of dilution, L_D , is

$$L_D = RT^2 \frac{d \ln p/p_0}{dT},$$

where p is the vapor pressure of the solution, and p_0 is the vapor pressure of the pure solvent at the same temperature. For a negative value of L_D , as in the case of potassium and sodium chlorides, the equation tells us that the ratio p/p_0 decreases with the temperature. Thus, if p/p_0 decreases with increasing temperature, it means that p increases more slowly than p_0 with the temperature, and from Raoult's law this would indicate that at higher temperatures there is an increase in the degree of ionization of the salt. A. A. Noyes⁵ found experimentally, however, that for salts of this type the opposite was true, namely that the degree of ionization actually decreased with the temperature. There must, therefore, be some factor which aids in determining what this value shall be, other than simple ionization. The heats of ionization can be obtained from a knowledge of the rate of change of the degree of ionization with the temperature, from the relation

¹ Berthelot and Hovvay, *Ann. chim.*, [5] 29, 318 (1885).

² Noyes and Falk, *THIS JOURNAL*, 33, 1455 (1911).

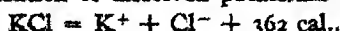
³ A. Werner, *Neuere Anschauungen u. d. Gebiete d. Anorg. Chemie.* (1913).

⁴ *Loc. cit*

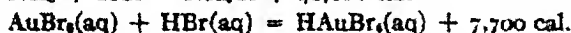
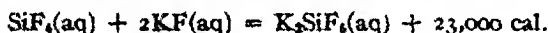
⁵ A. A. Noyes, *Carnegie Inst. Pub.*, 63, 339 (1907)

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}$$

The values calculated from this relationship, however, do not seem to agree with those observed. For instance, Arrhenius gives the energy equation for the ionization of dissolved potassium chloride¹ as



whereas, when calculated, the value of the heat of ionization is found to be $-2,000$ calories. According to Senter, "it seems that the process of ionization must be attended by some exothermic reaction which more than compensates for the heat presumably absorbed in splitting up the molecules." Van der Waals,² as well as Werner, has suggested that ionization in aqueous solution is essentially a hydration process and thus the energy necessary for its completion may come from the combination between the ions and water. The heats of ionization are small in comparison with the heats of hydration. Thomsen³ has found values as high as 8,000 calories per mol. of water combining to form a hydrate. Of the two effects, therefore, this one would predominate. The order of magnitude of the heats of formation of higher order complexes of mixed salts is also great enough to overshadow any ionization effect. A few examples are taken from Pattison Muir's, "Elements of Thermal Chemistry," Appendix I:



These heats are all positive. Now it will be noted in the curves in Figs. 4 to 7 that the deviations of the observed values from those calculated are always toward a larger negative heat. That is, with dilution, the complexes existing in the solution are broken up with the absorption of heat.

G. Summary.

1. The reversible molal heat of dilution has been determined for solutions of the single salts, sodium, potassium and strontium chlorides at various concentrations ranging from 3.2 wt. N to 0.2 wt. N , and also for solutions of the mixed salts $\text{NaCl} : \text{KCl}$, $\text{NaCl} : \frac{1}{2} \text{SrCl}_2$, $\text{KCl} : \frac{1}{2} \text{SrCl}_2$, and $\text{KCl} : \text{SrCl}_2$ for the above mentioned range of concentration.

2. The heats of dilution of sodium and potassium chlorides are negative. This fact in the light of the equation

$$L_D = RT^2 \frac{d \ln p/p_0}{dT},$$

¹ Senter, *Outlines of Physical Chemistry*, p. 344.

² Van der Waals, *Z. physik. Chem.*, 8, 215 (1891).

³ Pattison Muir, "Elements of Thermal Chemistry," p. 167.

in which L_D is the molal heat of dilution, indicates an increase in the degree of ionization with the temperature, contrary to the experimental results of A. A. Noyes, unless explained on the basis of the decomposition with dilution, of complexes existing in the solution.

3. The heats of dilution for the solutions of the mixed salts bear no simple additive relation to the heat effects of the single components at equivalent concentrations.

4. The results have been explained on the basis of the conception of higher order compounds as put forth by A. Werner.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF THE HEATS OF DILUTION OF SOLUTIONS OF BARIUM CHLORIDE AND BARIUM-SODIUM CHLORIDE MIXTURE.¹

By G. MCP. SMITH, ALLEN E. STEARN AND R. F. SCHNEIDER.

Received August 5, 1919.

In connection with some work done in this laboratory on the heats of dilution of mixed salt solutions of strontium chloride with certain of the alkali chlorides,¹ it was thought to be of interest to measure the reversible molal heats of dilution of solutions of barium chloride and of equivalent mixtures of barium and sodium chlorides, and thus to ascertain whether the results obtained in the case of strontium were unique. The behavior of the barium chloride solution itself would be of interest, inasmuch as the strontium chloride in solution behaves differently from the two uni-univalent salts, sodium chloride and potassium chloride. This is due, perhaps to the bivalent strontium and to its ionization in partial stages to intermediate ions such as the SrCl^+ ion. In concentrated solutions this intermediate ion is perhaps almost the only simple ionic form of the strontium.

The sodium and barium chlorides were of various brands, all labeled c. p. Previous work² along this same line as well as this work has shown that the heat effects in solutions as concentrated as 0.2 weight normal are so small as to be hardly measurable. Thus, inasmuch as small amounts of impurities have no effect on the results in this work, it was considered unnecessary to purify the salts further.

The apparatus used and the method of measurement were the same as in the work to be described in the next paper.³

¹ From a thesis submitted to the College of Liberal Arts and Sciences of the University of Illinois by R. F. Schneider in partial fulfillment of the requirements for the degree of Bachelor of Science, 1919.

² See Wells and Smith, in the February issue.

³ *Ibid.*

Experimental Data.

Tables I and II give the heats of dilution of the various solutions studied. For more complete detail regarding the data taken and the methods of calculation of the molal heat effects, see the previous paper.

TABLE I.—HEAT OF DILUTION OF BaCl_2 SOLUTIONS.

Concentration, Wt. N.	Solution, G.	Water of dilution Moles	Total heat of dilution cal.	Molal heat of dilution cal.	Reversible molal heat of dilution. cal.
3.2	10,000	35	-102.0	-2.9 ^a	
		35	-95.0	-2.7 ^a	
		25	-43.7	-1.8 ^a	-2.9 ^a
2.8	10,000	35	-26.75	-0.77	
		25	-22.0	-0.88	
		15	-15.3	-1.02	-1.20
1.6	10,000	35	-13.75	-0.394	
		20	-7.15	-0.41	-0.435

* These results are not to be relied on to any great extent, owing to the fact that at this concentration the solution is almost at its saturation point. The most probable indication of the value of the reversible molal heat of dilution is the first or second dilution giving a value of between -2.9 and -3.0 cal./mol.

TABLE II.—HEAT OF DILUTION OF $\text{NaCl} \cdot \frac{1}{2} \text{BaCl}_2$ SOLUTIONS

Concentration, Wt. N.	Solution, G.	Water of dilution Moles.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. cal.	
					Obs.	Calc.
3.2	10,000	35	-276.5	-7.89		
		25	-232.0	-9.3		
		15	-172.2	-11.48	-14.1	-10.25
1.6	10,000	35	-138.0	-3.94		
		25	-106.2	-4.25		
		15	-66.4	-4.50	-4.93	-3.98
0.8	10,000	35	-55.2	-1.57		
		25	-40.7	-1.63		
		15	-25.42	-1.69	-1.78	-1.50
0.4	10,000	40	-12.05	-0.30		
		25	-13.35	-0.38		
		15	-12.6	-0.50	-0.75	-0.78

Discussion.

Fig. 1 gives the graphical representation of the results of the heats of dilution as taken from the tables. Reversible molal heat effects are plotted as ordinates against concentration, expressed in weight normality, as abscissas.

The barium chloride curve seems to be divisible into two distinct regions; the one up to a concentration of about 2.5 N and the other up through the higher concentrations. Comparison with the curve for strontium chloride (see previous paper), which was much more thoroughly worked out experimentally, shows two regions perfectly analogous

¹ *Loc. cit.*

ents at their respective concentrations in the mixture. It is seen that with increasing concentration these two curves diverge more and more. For a more detailed discussion of this type of curve see the next paper. Briefly, this divergence seems explicable only on the assumption that with increasing concentration there is an increasing tendency to form higher order complexes between the various salt constituents due to their mass action. Thus, at low concentrations, where these complexes would be present only in small amounts, their specific effect should be negligible, and the two curves should tend to coincide. This is actually the case

Summary.

1. The reversible molal heat of dilution has been determined for solutions of barium chloride of 3.2, 2.8, and 1.6 weight normal, and for solutions of the mixed salt $\text{NaCl} : 1/2 \text{BaCl}_2$ at 3.2, 1.6, 0.8, and 0.4 weight normal.
2. The heats of dilution of the mixed salt bear no simple additive relation to the heat effects of the simple components at equivalent concentrations.
3. The behavior of barium chloride in this respect is found to be analogous to that of strontium chloride.
4. These results can be explained on the same basis as the results obtained with the mixed strontium salts, namely on the basis of the formation of higher order compounds.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BROOKLYN POLYTECHNIC INSTITUTE.]

THE SEPARATION OF ZIRCONIUM AND TITANIUM AS THE PHOSPHATES.

BY JAMES BROWN AND H. T. MADDEN.

Received September 2, 1919.

In a previous paper,¹ one of us made use of the Hillebrand method² of separating zirconium from titanium by precipitation of the former by use of hydrogen peroxide and alkaline phosphate in a faintly acid solution. The titanium, when large in amount, was determined as a difference or by the permanganate method, and by the colorimetric method when small amounts were present. The work recorded in the present paper was undertaken with the object of making a direct gravimetric determination of the titanium in the filtrate from the zirconium phosphate precipitation.

The standard solutions employed were prepared from pure potassium zirconium fluoride (K_2ZrF_6), and from pure potassium titanium fluoride

¹ THIS JOURNAL, 39, 2358 (1917).

² "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.*, 422, 141 (1910).

(K_2TiF_6), respectively. The pure salts of commerce were recrystallized from boiling water several times, and were then converted into the sulfates by evaporation with sulfuric acid in a platinum dish until all fluorine was expelled. The residues were diluted with water. Qualitative tests showed the absence of iron, aluminum, manganese, and rare earths from both solutions.

Standardization of Solutions.

The solutions of zirconium sulfate and of titanium sulfate thus prepared were standardized by precipitation with ammonia and ignition to the dioxide, in the usual way.

From other portions of the zirconium solutions, the base was precipitated as the phosphate, by disodium or diammonium phosphate, the solution containing 1-2% by volume of sulfuric acid. The zirconium phosphate was filtered off, washed, ignited and converted to the dioxide as follows: It was fused with sodium carbonate, the melt leached with water, and the insoluble residue dissolved either in hydrochloric acid or by fusion with sodium bisulfate and subsequent treatment with a dilute solution of sulfuric acid. The zirconium phosphate showed marked decrepitation during ignition. The zirconium was precipitated with ammonia, and weighed as ZrO_2 after ignition. The zirconium dioxide thus obtained from the phosphate corresponded in each case with the standard obtained by treating the original solution with ammonia. The amount of zirconium dioxide involved varied from 0.1608 to 0.3216 g. In view of the qualitative and quantitative checks thus obtained, the zirconium sulfate solution was considered free from interfering bases.

The solution of titanium sulfate, standardized by precipitation with ammonia, and ignition to titanium dioxide, was further standardized as follows:

Portions of the solution containing 1-2% of sulfuric acid by volume were precipitated by use of disodium or diammonium phosphate, filtered, ignited and weighed. The titanium phosphate thus obtained was of variable composition. It was, therefore, converted to the dioxide as with zirconium, and weighed as titanium dioxide. The dioxide thus obtained corresponded to the standard obtained by use of ammonia directly with the original solution. The titanium dioxide used varied from 0.1124 to 0.5726 g.

As a further check on the titanium solution, titanium was determined by reduction with zinc and sulfuric acid, addition of an excess of ferric sulfate, and titration of the reduced iron salt by use of permanganate.¹ The results thus obtained agreed very well with the standard obtained by use of ammonia alone, and the titanium solution was judged free from interfering bases.

¹ Newton, *Am. J. Sci.*, [4] 25, 130 (1908).

Separation of Zirconium and Titanium.

Measured amounts of the solutions of zirconium and titanium sulfates were mixed and made acid to the extent of 1-2% of free sulfuric acid by volume. An excess of hydrogen peroxide was added. A solution of disodium or diammonium phosphate was added in excess, and the solution allowed to stand overnight. The precipitated zirconium phosphate was filtered off and washed with water containing a few drops of sulfuric acid and hydrogen peroxide. The zirconium precipitate is colored yellow by titanium. To remove this titanium we proceeded as directed by Hillebrand¹ by fusing with sodium carbonate, leaching, and redissolving by fusion with sodium bisulfate and action of dil. sulfuric acid. The zirconium was reprecipitated by hydrogen peroxide and phosphate, allowed to stand, filtered and washed. In some cases this second zirconium precipitate contained small amounts of titanium, which were removed by repeating the above treatment.

The zirconium phosphate precipitated was converted to zirconium dioxide, as in the standardization, and weighed as such. The results for the zirconium are given in the table.

The combined filtrates from the zirconium phosphate precipitation were heated to get rid of the hydrogen peroxide. The volume of the solution was then adjusted so that the content of sulfuric acid was about 2% by volume, and disodium or diammonium phosphate solution was added to assure an excess. The liquid was allowed to stand about one hour, and the precipitate filtered and washed. The precipitate was converted to titanium dioxide as in the standardization and weighed as such.

The results are given in the following table:

ZrO ₂ taken G.	TiO ₂ taken. G.	ZrO ₂ found. G.	Error G.	TiO ₂ found G.	Error. G.
0.1287	0.0562	0.1282	-0.0005	0.0556	-0.0006
0.1287	0.0562	0.1281	-0.0006	0.0559	-0.0003
0.2594	0.0562	0.2588	-0.0006	0.0560	-0.0002
0.2594	0.1124	0.2592	-0.0002	0.1120	-0.0004
0.2594	0.1124	0.2585	-0.0009	0.1118	-0.0006
0.1287	0.1124	0.1284	-0.0003	0.1121	-0.0003
0.2594	0.0562	0.2591	-0.0003	0.0556	-0.0006
0.2594	0.0562	0.2592	-0.0002	0.0558	-0.0004
0.2594	0.1124	0.2589	-0.0005	0.1121	-0.0003

Summary.

The separation of titanium and zirconium by the Hillebrand method is quantitative, within the limits used in this work. The zirconium phosphate is converted to the dioxide and gives accurate results. The titanium in the filtrate from the zirconium phosphate may be completely precipitated by the use of sodium or ammonium phosphate, but as this precipi-

¹ *Loc. cit.*

tate is of variable composition, it should be converted to the dioxide to obtain quantitative results.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF QUEEN'S UNIVERSITY.]

THE ANALYSIS OF ACETONE BY MESSINGER'S METHOD.

By LEO FRANK GOODWIN.

Received September 22, 1919.

In the course of research work extending over the last 6 or 7 years, it was frequently necessary to make accurate determinations of acetone both in large and small amounts. Messinger's method¹ was found to give concordant results under all conditions, and since its accuracy has been disputed by one or two workers, and upheld by others, a résumé of the work on the subject and conclusions are herewith presented.

Since the publication of the original Messinger method, it has been subjected to an extended critical examination by Collischonn,² Edward R. Squibb³ and L. F. Kebler.⁴ Perhaps the only fault with all this work lay in the fact that no special precautions were taken to obtain pure acetone, and that the acetone was never weighed out accurately. Since, however, it was desired only to work out the conditions under which concordant results could be obtained, this hardly mattered.

Messinger's method has been seriously criticized only by Vaubel and Scheurer,⁵ and by Geelmuyden.⁶ The statements of the former authors were conclusively refuted by Keppeler,⁷ and those of the latter by Marriott.⁸

Messinger's original results were carried out to an accuracy of only one part in 200. Collischonn² made very accurate experiments, but used only a sample of Kahlbaum acetone purified through the bisulfite compound, which distilled within 1°. He carried out other experiments with commercial acetone and showed that concordant results could be obtained.

Squibb and Kebler used sodium hypochlorite solutions, but appear to

¹ *Ber.*, 29, 3336 (1888). Other papers on the determination of acetone, not elsewhere referred to, are as follows: G. Kraemer, *Ber.*, 13, 1000 (1880); E. Hintz, *J. Soc. Chem. Ind.*, 7, 459 (1888); L. Vignon, *Ibid.*, 9, 639 (1890); E. Arachesquene, *Ibid.*, 9, 660 (1890); Otto Folin, *J. Biol. Chem.*, 4, 177 (1917); T. Stuart Hart, *Ibid.*, 4, 477 (1918); J. Rakshit, *Analyst*, 41, 246 (1916).

² *Z. anal. Chem.*, 29, 562-572; *J. Soc. Chem. Ind.*, 10, 166 (1891).

³ *THIS JOURNAL*, 18, 1068-1079 (1896).

⁴ *Ibid.*, 19, 316-320 (1897).

⁵ W. Vaubel and C. Scheurer, *Z. angew. Chem.*, 18, 215-216 (1905).

⁶ H. Chr. Geelmuyden, *J. Chem. Soc.*, 70, 679 (1896).

⁷ G. Keppeler, *Z. angew. Chem.*, 18, 464-465 (1905).

⁸ W. M. Marriott, *J. Biol. Chem.*, 16, 281 (1913).

⁹ *Loc. cit.*

have made up their solutions by putting the weighed acetone directly into water contained in an open beaker and diluting. Their method which is claimed to be an improvement on the original one of Messinger, does not appear to have been adopted elsewhere.

As will be seen from the experiments recorded herewith, Messinger's method gives accurate results if carried out with the precautions specified by Collischonn. The influence of shaking, excess acid, and time of standing seems not, however, to have been fully investigated previously.

Analysis of Acetone by Messinger's Method.

The following procedure, which is practically the standard method recommended everywhere, if strictly adhered to, gives accurate and consistent results.

An amount of acetone in aqueous solution, equivalent to 30-40 mg. is pipetted or added to 50 cc. of *N* sodium hydroxide solution contained in a glass bottle which can be closed with a ground glass stopper. After standing for 5 minutes, about 25% excess of a 0.1 *N* solution of iodine is run in from a buret with continual shaking. It is essential to shake properly or to keep the liquid in continuous rotation. The excess of iodine is needed to complete the reaction.¹ The bottle is then stoppered and the solution allowed to stand for at least 10 minutes (20 minutes in cold weather).

Twenty-five cc. of 2 *N* sulfuric acid is then added from a measuring cylinder, 0.3-0.4 cc. being added in excess of the amount found necessary to neutralize the 50 cc. of caustic soda solution. A 0.05 *N* solution of sodium thiosulfate is then added from a buret until the yellow color just remains visible. Freshly prepared starch solution is now added and the titration finished. 1 cc. of 0.1 *N* iodine = 0.96747 mg. of acetone.

If a larger excess of sulfuric acid is added, too much thiosulfate is required, and the real amount of iodine solution required is thus reduced (see below).

If the bottle is not shaken vigorously while adding the iodine solution, the iodine cannot act completely on the acetone, and as much as 3 times the ordinary amount of thiosulfate may then be required to neutralize the iodine left uncombined, it being transformed into iodate.

The above method of procedure is based on the following experiments:

Method of Preparation of the Acetone Solutions.—750 cc. of British Government acetone was fractionated through a 12-bulb Young still-head, and the main fraction which distilled at 56.07-56.08° at 761.1 mm. used for analysis.

In preparing acetone solutions it is impossible to pipet out the acetone, or even to weigh it into a beaker containing water as done by Squibb. Loss of acetone cannot be avoided under such conditions. The method

¹ Collischonn, *Loc. cit.*

employed was to take a calibrated, graduated flask and weigh it while partly filled with water and stoppered. The acetone was delivered into the flask, this shaken and again weighed for the acetone. The flask was then filled to the mark with water and aliquot portions were withdrawn with carefully standardized pipets.

A 36.25% solution of acetone by weight was thus prepared, and of this 5.022 cc. was pipetted out and diluted in another graduated flask to 250 cc.

The thiosulfate and iodine solutions were standardized against each other every 2 or 3 days, and at least once a week against a standard solution of sodium or potassium iodate. Slight changes in strength were, therefore, always allowed for. All pipets, graduated flasks and burets were calibrated several times, and the corrections applied during the work.

The Reproducibility of the Results.

The constancy of results obtained by Messinger's method was first tested. For this purpose 5.022 cc. of the acetone solution prepared as above was pipetted out into glass bottles and analyzed according to the method described. 50 cc. of *N* caustic soda was used, and neutralized for the back titration with 24.4 cc. of sulfuric acid, this being 0.4 cc. in excess. The experimental results obtained were as follows:

TABLE I
Experiments to Test Concordance

Expt	0.1 <i>N</i> iodine Cc.	0.05 <i>N</i> thio- sulfate calculated as 0.1 <i>N</i> iodine Cc.	0.1 <i>N</i> iodine used Cc.
11 .	40.19	4.08	36.11
12 .	40.19	4.00	36.19
13 . .	45.20	9.21	35.99
14 . . .	45.20	9.29	35.91
16 . . .	45.20	8.98	36.22
17 . . .	45.20	9.11	36.09
18	45.20	8.95	36.25
19	45.20	9.05	36.13

Mean, 36.11

It is seen that Messinger's method gives closely concordant results.

On the basis of Expts. 13 and 14, assuming the specific gravity of a 36.25% solution of acetone to be 0.9549, the purity of the acetone would be 97.6%. The iodine solution was 0.09788 *N*. Expts. 16 and 17 give 98.00%; the iodine solution here was 0.09770 *N*.

In common with previous investigators, the difference from 100% was assumed to be water, and a solution thus prepared was used to test Messinger's method further.

Influence of Shaking.—Shaking has a noticeable effect, and experiments were, therefore, run in which the iodine solution was added from a buret to the alkaline acetone solution, without shaking. The stoppered

bottle was then shaken occasionally, or sometimes only rarely, so as to vary the conditions as much as possible. The following results were obtained. The iodide acetone solution stood for 20 minutes before being acidified, and in Expts. 7 and 8 for 35 minutes.

TABLE II.
Discordant Results Obtained if Shaking is Omitted.

Expt.	0.1 N iodine Cc.	Thiosulfate equivalent 0.1 N iodine. Cc.	Net 0.1 N iodine. cc.
2.....	45.20	11.32	33.88
3.....	45.20	16.27	28.93
4.....	45.20	15.69	29.51
5.....	40.19	11.06	29.13
6.....	40.19	8.82	31.37
7.....	40.19	11.80	28.39
8.....	40.19	13.75	26.44
9.....	40.19	10.32	29.87
10.....	40.19	11.00	29.19
15.....	45.20	16.07	29.13
20.....	40.19	11.76	28.43

Table II shows that unless the iodine solution is added with continual shaking the results are very discordant.

Influence of Time of Standing.—The effect of time of standing before acidifying with sulfuric acid was next studied. For this purpose a fresh solution of acetone, purified with permanganate and distilled, was made up, containing 4.185 g. in 100 cc. of which 25.026 cc. was diluted to 250 cc. and 5.022 cc. pipetted out for analysis. The following results were obtained:

TABLE III.
Influence of Time of Standing Before Acidifying.

Expt.	0.1 N iodine. Cc.	Thiosulfate equivalent 0.1 N iodine. Cc.	Net 0.1 N iodine used. Cc.	Time of standing. Min.
53.....	35.17	12.94	22.23	20
54.....	35.17	12.91	22.26	20
55.....	35.17	12.88	22.29	20
51.....	35.17	12.94	22.23	5
52.....	35.17	12.87	22.30	5
56.....	35.17	12.87	22.30	5
57.....	35.17	12.93	22.24	5

Mean, 22.26

Five minutes standing is, therefore, sufficient, as has already been pointed out by previous experimenters, although 20 minutes does no harm. My practice is to let solutions stand for 20 minutes, since in cold weather the reaction takes a longer time for completion.

Another point in this connection required elucidation. For some reason previous experimenters, in their directions for making the analysis, have specified that after adding the acetone to the caustic soda solution, the

solution should stand for 5 min. I had supposed that there might be some reason for this, since alkalis effect a change to di-acetone,¹ but experiments were finally made to clear up this point. In one analysis run as usual, the net iodine used was 22.93 cc. A similar experiment in which the iodine solution was added to the acetone caustic soda solution directly after mixing gave the net amount of iodine used as 22.93 cc. It would, therefore, appear to be unnecessary to wait for 5 minutes before adding the iodine solution.

Effect of Varying Amounts of Acid on the Titration.—When excess of acid is used a larger amount of thiosulfate solution is required for the back titration. The following experiments make this point clear:

Blank experiments were run by adding a known amount of iodine solution to the caustic soda, letting stand for 20 minutes, acidifying and titrating back. The 50 cc. of *N* caustic soda used required 23.9 cc. of sulfuric acid for neutralization.

TABLE IV.
Effect of Varying Amounts of Sulfuric Acid.

Expt.	0.1 <i>N</i> iodine taken. Cc.	2 <i>N</i> sulfuric acid Cc.	0.1 <i>N</i> iodine used. Cc.	Excess thiosulfate as 0.1 <i>N</i> iodine. Cc.
3A.....	7.07	26.0	7.24	+0.17
4A.....	7.07	27.0	7.28	+0.21
5A.....	7.07	25.0	7.17	+0.10
6A.....	7.07	25.5	7.22	+0.15
7A.....	7.07	24.0	7.11	+0.04
8A.....	8.08	24.1	8.08	0.00
9A.....	10.10	25.0	10.10	0.00

To get accurate results it is, therefore, advisable to use about 0.5 cc. excess of 2 *N* sulfuric acid.

Expts. 8A and 9A show that there was no nitrite or alcohol in the caustic soda used.

TABLE V.
Effect of Using a Stopped Bottle or an Open Flask.

Expt.	Conditions	0.1 <i>N</i> iodine. Cc.	Thiosulfate equivalent to 0.1 <i>N</i> iodine. Cc.	Net 0.1 <i>N</i> iodine used. Cc.
7B.....	Stopped bottle	28.48	7.40	21.12
8B.....	Stopped bottle	28.62	7.52	21.14
9B.....	Stopped bottle	28.17	7.17	21.14
10B.....	Stopped bottle	35.30	14.17	21.13
				Mean, 21.13
11B.....	Open flask	29.59	8.90	20.74
12B.....	Open flask	30.17	9.64	20.56
13B.....	Open flask	28.46	7.80	20.70

Mean, 20.67

¹ A. Hoffman, THIS JOURNAL, 31, 723 (1909).

In experiments undertaken some 6 years ago when acetone determinations of not as high a degree of accuracy had to be made, the titrations were carried out in an open bottle. It seemed of interest to determine the error thus introduced. The preceding results were obtained.

The results show that less iodine is required when an open flask is used. This was confirmed by another series of experiments run in the same manner in which the mean of 5 determinations in an open flask was 20.43 cc. iodine, as against a mean of 20.71 cc. for 3 experiments carried out in a stoppered bottle.

The Influence of Dilution.—W. M. Marriott¹ has recently published experiments showing that accurate results can be obtained even at great dilution. My own experiments lead to the same conclusion, and I, therefore, refrain from quoting any further evidence on this point.

The Influence of Methyl and Ethyl Alcohol.—Previous investigators had always assumed that methyl alcohol was without influence on the titration, although they recognized that ethyl alcohol had some influence.

Rakshit² worked out a method for estimating acetone in presence of ethyl alcohol, and found that this could be done with accuracy if lime water or barium hydroxide was used instead of caustic soda in the Messinger method. He makes a correction of 0.8 cc. of 0.2 *N* iodine solution for each one cc. of ethyl alcohol present. He states that the method can be used with as many as 10 parts of ethyl alcohol to one part of acetone. He found also that one cc. of methyl alcohol has no effect on his method. Kebler³ found that one cc. of ethyl alcohol required a correction of 0.8 cc. of 0.1 *N* iodine. The experiments listed below show that a certain error is introduced by the presence of methyl alcohol. Experiments were run as usual, but with the addition of 0.5 cc. of pure methyl alcohol. Expt. 97 was a blank. The methyl alcohol used in Expt. 98 had been dried with lime and redistilled.

TABLE VI.
Influence of Methyl Alcohol

Expt.	0.1 <i>N</i> iodine Cc	Thiosulfate equivalent 0.1 <i>N</i> iodine Cc	Net 0.1 <i>N</i> iodine used. Cc
97..	10 10	0.04	0 06
91	10.10	9.78	0.32
92	10 10	8 36	1.74
93	10 10	9.69	0.41
94 ..	10 10	9 50	0 60
97 .	10 30	9 74	0 56
98 .. .	10 30	9.84	0.46

It may be concluded that 0.5 cc. of methyl alcohol causes an error of nearly 0.5 cc. in the amount of 0.1 *N* iodine solution used.

¹ *Loc. cit.*

² Jitendranath Rakshit, *Analyst*, 41, 246 (1916).

³ Kebler, *Loc cit*

When the present paper was nearly completed, a short note by A. J. Field¹ was found. He states that Collischonn's method is unsatisfactory, but quotes no experimental evidence, and his failure to obtain concordant results is probably due to non-observance of the precautions to be adopted, and more possibly due to adding varying amounts of acid for the back titration. He states, however, that "if after the addition of the iodine solution, the mixture is shaken for 5 minutes, a low result is obtained, while shaking for 20 minutes gives a higher result, the percentage varying with the length of time of agitation." This is quite contrary to the experiments recorded above, but two additional experiments were nevertheless run to test the point. An acetone solution was titrated, the iodine solution being added to the acetone caustic soda solution, without shaking, and the stoppered bottle was then shaken vigorously while standing, for 5 minutes, and for 20 minutes, respectively. The net amounts of iodine used were identical—22.26 and 22.26 cc. The theoretical amount of iodine used when carrying out the titration under the conditions specified in this paper, that is, running in the iodine solution with continual agitation, was 22.26 cc.

Summary.

- (1) It has been shown that Messinger's method for the analysis of acetone gives accurate and concordant results under proper conditions.
- (2) The influence of standing, method of adding the iodine solution and shaking, effects of excess acid, and dilution have been studied and found not to influence the results under proper conditions.
- (3) Methyl alcohol and ethyl alcohol both use up a certain amount of iodine solution.

KINGSTON, ONTARIO.

[CONTRIBUTION FROM THE MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

A SIMPLE HYDROGEN ELECTRODE.²

By C. H. BAILEY.

Received September 25, 1919

The considerable number of hydrogen electrodes that have been described in the literature suggests either that these devices have not been wholly perfected, or that electrodes suited to one purpose may not be adapted to other uses. Moreover, several of the forms that have been proposed are expensive; most of them are somewhat complicated and fragile and their construction presents an impossible undertaking for the average amateur glass blower.

This laboratory has had occasion to make a large number of hydrogen-

¹ *J. Ind. Eng. Chem.*, 10, 552 (1918).

² Published with the approval of the Director as Paper No. 180, of the Journal Series of the Minnesota Agricultural Experiment Station.

ion determinations, especially of the water extracts of plant material. Several types of electrodes have been tried, and most of them laid aside as being unsuited to this purpose. In the first place, certain of our preparations were so low in electrical conductance as to diminish the sensitivity of the potentiometer set-up. This was due to the considerable distance in most types of electrodes between the platinized electrode and the point of contact with the saturated potassium chloride solution as well as to the manner of making this contact. Again, as stated by McClendon and Sharp,¹ the platinized electrodes should be wholly immersed in the extract, and with certain electrodes this could be accomplished only by tipping them at an awkward angle, making even more difficult the contact with the potassium chloride solution. It appeared desirable to develop, if possible, an electrode which would be simple in construction and operation, have a short interval between platinized electrode and contact with the potassium chloride solution, and permit of complete immersion of the platinized electrode.

After several trials an electrode was constructed which appeared to meet all these requirements. As shown in Fig. 1, it is made by blowing

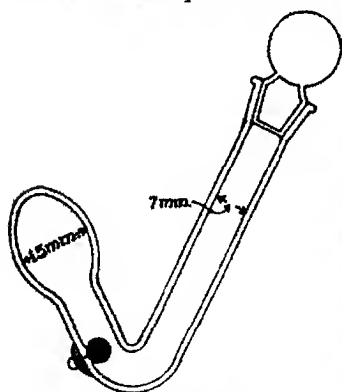


Fig. 1.—Cross-section of a simple hydrogen electrode

a small bulb in the closed end of a 7 mm. tube, which is then bent at the angle shown, about 50 mm. below the top of the bulb, and fitted at the open end with a solid glass stopper. Spare stoppers of about this size can be found in most well-established laboratories. Those which taper considerably are preferable. A gas-carbon mold is made which is slightly smaller than the stopper, and the glass at the open end of the tube is softened and flowed about the mold until it has approximately the correct internal dimensions. The stopper is then ground into its seat by the use of a mixture of

carborundum powder (150 mesh), turpentine and camphor.

The metal electrode is made by cutting a round piece of thin gold plate 5 mm. in diameter. Such gold plate is obtainable from dental laboratories and is preferable to platinum foil since the time for saturation with hydrogen ions is comparatively short. To this is soldered with gold a piece of No. 30 (0.010 in.) platinum wire about 15 mm. long. This can be done by carefully heating the middle of the wire in a small flame, and melting on one end a small bit of the pure gold foil previously cut in a strip and bent about the end of the wire. This gold is then heated just to

¹ *J. Biol. Chem.*, 38, 534 (1919).

a molten state, the round bit of foil placed under it, and the two pounded together by tapping with a light hammer. The gold used as solder, and the portion of the wire nearest the foil, are then beaten thin.

The opening in the tube through which the wire lead from the electrode passes is then prepared. This is most conveniently done by heating a piece of No. 18 platinum wire about 2 cm. from the end, and holding it against the tube. The hot wire can be gradually forced through the glass wall, leaving a small, smooth opening. It is not difficult to then maneuver the wire lead of the metallic electrode through the hole thus prepared. Low melting-point or soft glass can be flowed in around the wire, completing the mechanical part of the job.

No. 25 (0.018 in.) platinum wire can be used for the lead and external contact, if it is plated with gold and beaten thin near the foil. The electrode is drawn well into the glass at the time the soft glass is fused in around the wire. In this way there are no heavy platinum parts exposed within the tube, and consequently no delay due to the slowness with which such parts are saturated with hydrogen ions. The heavier platinum wire which passes out through the glass wall is more substantial than fine wire and less apt to break off close to the glass.

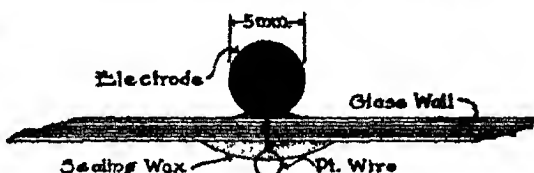


Fig. 2.—Detail of metallic electrode and connections.

A convenient way of reinforcing the platinum lead wire outside the tube is shown in detail in Fig. 2. The wire is bent forward for a short distance, then curved in a loop, and finally bent back close to the glass. The lower part of the loop and loose end of the wire are surrounded with a small lump of sealing wax, which must adhere tightly to the glass tube. Metallic connection to the potentiometer can easily be effected by catching a small hook at the end of a coiled copper wire to the open end of the platinum loop just without the sealing wax. Electrodes thus prepared have appeared more rugged than those in which the free end of the wire has not been secured. If the wire breaks in will generally be at the outer surface of the sealing wax, and by paring the latter, contact may be established with the free end of the wire previously embedded in the wax; and the electrode thus used for a considerable time.

The gold foil is platinized in the customary way, and the electrode is used in the following manner. Sufficient of the liquid under examination is placed in the open arm to completely fill it. The tube is then tilted so that the liquid flows into the bulb end, displacing the air. This is repeated until the bulb arm is completely filled, and the open arm to a depth of about 10 mm. above the top of the bend. A slender glass tube

leading from the hydrogen generator or tank is then placed in the open arm so its lower end about reaches the lower part of the bend, and hydrogen is gently bubbled into the bulb, displacing the liquid, which rises in the open arm. Sufficient hydrogen is admitted to fill the closed arm. If the open arm is not level full of the liquid, it is completely filled, and the stopper carefully seated in such a manner as to permit the excess liquid to be forced out as it is inserted. All air is thus excluded from the tube. It is vigorously shaken for two minutes and then tilted so enough liquid flows into the closed arm to just cover the foil. The stopper is removed, and by a series of quick flips part of the liquid in the open arm is thrown out. The outer surfaces of the tube are then rinsed with distilled water and dried.

To complete the circuit the platinum wire loop is connected to the potentiometer as previously described, while a slender siphon tube filled with saturated potassium chloride solution is dipped into the open arm. This siphon is made by drawing out one end of a 3 mm. (i. d.) glass tube to a slender tip about 10 cm. long. The tube is bent to a V shape just above the tip, and the large end cut off to a length of about 6 cm. The completed siphon is filled with saturated potassium chloride solution, and finally several fragments of filter paper, previously soaked in potassium chloride solution, are forced into the fine tip by means of a needle. This filter paper prevents the potassium chloride solution from actually siphoning over to an appreciable extent while the readings are being taken. The tip can be brought very close to the platinized foil, thus reducing the electrical resistance of the cell. The other end dips into a vessel filled with saturated potassium chloride solution, which in turn is connected to the calomel electrode. This scheme is adapted from the suggestions made by Van Slyke and Baker.¹

Hydrogen electrodes made and used as described have proven very useful in determining the hydrogen-ion concentration of water extracts of foods, such as wheat flour. It comes to equilibrium promptly, and is easy to fill and clean. About 10 cc. of the extract is sufficient to rinse and fill the cell, and even less may be made to serve if care is taken. When used with the potentiometer in this laboratory the complete set-up is sensitive to 0.25 millivolt.

The writer's obligations to Dr. R. A. Gortner for his services in constructing several of these useful electrodes are gratefully acknowledged.

ST. PAUL, MINNESOTA.

¹ L. L. Van Slyke and J. C. Baker, N. Y. (Geneva) Sta. *Technical Bull* 65 (1918).

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE COMPRESSIBILITY OF INDIUM.

BY THEODORE W. RICHARDS AND JITSUSABURO SAMESHIMA.

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In a paper¹ collating recent values of the compressibilities of the elements, the periodic nature of compressibility was emphasized, especially in relation to the similar periodicity of other properties. In this connection, the values of these constants for indium and gallium are particularly interesting because of the low melting points of these substances. The compressibility of gallium has already been determined;² that of indium is recorded in the present paper.

The sample of metal used in the following determinations had been carefully purified, having been recovered by suitable electrolytic means from the amalgams used in an earlier electrochemical research.³ It was cast in the shape of a cylindrical bar by slowly cooling liquid indium in an appropriate glass tube which had been coated with an exceedingly thin film of soft paraffin to prevent the adhesion of the metal to the glass. After cooling, the tube was broken and the ingot was removed, freed from traces of oxide and imperfections in casting at the upper end by cutting with a clean knife, and thoroughly cleansed from paraffin. The metallic rod thus obtained was 4.5 cm. long and 0.51 cm. in diameter and weighed about 6.7 g. The density of this bar was measured, in order to be sure that it contained no air cavities, by weighing first in air and then in water, suspended by a very thin wire, for which due allowance was made in the calculation. Two determinations gave the following results at room temperature:

Weight of indium.	6.6928	6.6903
Volume of indium.	0.9145	0.9152
Density of indium (20°)	7.318	7.310

A previous determination of this material (less carefully cast) gave the value 7.277.⁴

The method employed for the determination of the compressibility was in principle the same as that employed in most of the earlier work published from this laboratory. It has been often described, but a brief recapitulation is needful, in order that important improvements adopted in the present instance may be understood. A glass piezometer containing mercury is provided with a finely pointed platinum wire to make exact electrical contact with the meniscus forming the outer surface of the mercury in a tube of 1.5 mm. diameter. Successive weighed portions of mer-

¹ T. W. Richards, *THIS JOURNAL*, 37, 1643 (1915).

² Richards and Boyer, *Ibid.*, 41, 133 (1919).

³ Richards and Wilson, *Carnegie Inst. Publications*, 118 (1909).

T. W. Richards, *Ibid.*, 118, 13 (1909).

cury added to the mass demand, of course, successively higher and higher pressures to force the mercury down to the exact contact-point.

Thus a curve, giving the relation of added weights of mercury to added pressure, is easily established. This having been done, the substance to be studied is immersed in the mercury, displacing some of that liquid, and a new similar curve is established. From these two curves the difference between the compressibility of the substance and that of mercury is readily computed. The compressibility of mercury being known, the datum sought becomes known likewise.

In the present case, since indium amalgamates very readily, the solid metal cannot be plunged directly into the liquid one, but must be protected by an inert liquid (*e. g.*, water) which complicates the situation because of its far greater compressibility. The complication was largely neutralized with the help of an innovation introduced in the present case. By placing as nearly as possible the same amount of water in the piezometer during the initial measurements with mercury alone as is used afterwards to protect the indium, the final data were made practically independent of the compressibility of water, only a very small correction for a slight surplus or deficiency of this substance being required. Even this small correction was necessary merely because of the difficulty of making the quantities of water exactly identical. Practically, the indium simply displaced its volume of mercury, without coming into contact with it.

The consistent use of water had another even more important advantage; it made possible the employment of a much smaller piezometer, which (considering the very small quantity of indium at our disposal) greatly reduced the possible errors due to pressure-hysteresis in the glass, and to imperfections in the stopper of the piezometer. The glass vessel was made to fit closely the little bar of indium. The stopper, being only 0.55 cm. in diameter instead of over twice as much, could be fitted with great nicety. The instrument is shown in its actual dimensions, in the diagram. Such a small piezometer cannot be used with mercury alone since the compression of this quantity of the metal at 500 atmospheres is not enough to free the platinum point and obtain a satisfactory "make-and-break" contact. With a gram of water present the little instrument functioned admirably; the pressure of the "make" was only $\frac{1}{2}$ atmosphere less than that at the "break," and was doubt-



less much nearer than this (probably within 0.1 atmosphere) to the true value.

For small amounts of material, this device is perhaps even better than the elaborate steel piezometer¹ used in other recent work. The latter, to be sure, overcomes entirely the possible error due to hysteresis, but is no less subject to difficulties as regards the stopper than the glass piezometers, and can hardly be constructed on a diminutive scale commensurate with the small quantity of available indium.

The pressure gage was an absolute one,² of which the perfectly cylindrical plunger was found by careful measurement to possess a diameter of 0.25045 in., corresponding to an area of cross section of 0.31784 sq. cm. Thus, for example, a total weight on the piston of 166.820 kg. indicated a pressure of 514.7 megabars.³

The initial pressure used in the calculation was as usual 100 megabars—which is high enough to deprive possible minute air bubbles of most of their deleterious effect; and the final pressure was 500 megabars. In order to find the exact amount of added mercury needed between these limits, each curve showing the relation of pressure to weight of mercury was plotted on a large scale. The exact delineation of the curve near its extremities—usually a somewhat uncertain matter—was accomplished by a convenient device which may be of use in other cases.

A long, straight, flexible, uniform, rubber spline was bent, *by means of forces applied at the extreme ends*, so as to fit all the points. The curve being different in curvature at the two ends, the needful forces were of course different. Thus tendencies producing curvature, which cannot be very different from those causing the known part of the curve, were carried out beyond the extreme known points. The spline was light in weight, and with care was guarded against any considerable deforming effect of friction on the coordinate paper. The method was satisfactorily tested with known almost linear curves of the type at present concerned; with curves much more strongly bent it still yields fairly good results;⁴ and for interpolated points near the ends of the curve it appears to be the best graphic method. Even when the two ends of the curve are quite different in curvature, the method serves well, provided, of course, that at least 4 points are known. With curves of a definite type, like these, 3 points serve sufficiently well if the extrapolation is moderate in extent and the relative forces needed for the ends are known empirically. The idea of exerting different bending forces on the two ends is essentially similar to

¹ Richards and Bartlett, *THIS JOURNAL*, 37, 470 (1915).

² Richards and Shipley, *Ibid.*, 38, 989 (1916).

³ A megabar is the pressure of a megadyne per sq. cm. or 0.987 "atmosphere."

⁴ For example, the logarithms of 2,500, 3,000, 3,500 and 4,000 were plotted in relation to the numbers. Extrapolation by this method gave the value 0.611 as the logarithm of 4.1 instead of the true value, 0.613.

that of the excellent curve-ruler of Lord Berkeley;¹ but he did not emphasize the usefulness of the device for extrapolation. Possibly others have done so, but we have not found reference to this point.

The readings on the coördinate paper were verified by calculation based upon the slopes of tangents to the curves at appropriate points midway in the stretches to be spanned.

The compressibility of indium was computed as follows:

let w = weight of added mercury needed for the range 100–500 megabars when indium, water and mercury were all present

w' = weight of added mercury for the same range when only water and mercury were present

w_1 = difference in weights of water present under these two circumstances

W = weight of indium

D = density of indium.

0.2069 = constant increase in the weight of added mercury over this range, due to the substitution of 1 000 g of water for its volume of mercury

5425 = 400 times the density of mercury at 25° under 500 megabars pressure

β = the compressibility of indium

β' = 0.0000400, = the compressibility of mercury at 25° between 100 and 500 megabars²

Then

$$\beta = \frac{(w - w' - Kw_1)/D}{5425 \times W} + \beta'$$

Taking for example the first pair of measurements below (Expts 1 and 2)

$$= \frac{(0.1973 - 0.2082 - [-0.207 \times 0.0216])}{5425 \times 6.693} + 0.00000400 = 0.00000270$$

There follow all the necessary data, and the corresponding results are recorded in the last column.

Thus the compressibility of indium at 25° is seen to be 0.0000027, or about $\frac{2}{3}$ of that of mercury.

The experimental work may be verified by comparing the trials in which no indium was present, and among which therefore the differences should be due solely to the varying amounts of water. This comparison is reasonably satisfactory. The respective weights of water present in Expts. 1, 3, 5, 7 were 0.9463, 0.9309, 0.9235 and 1.0025, that is to say, the excesses of water above that in Expt. 5 (which contained least) were, respectively, 0.0228, 0.0074, 0.0000 and 0.0890. Multiplying each of these figures by the quantity 0.207 (the necessary amount of added mercury for one gram of water) and subtracting the products from the amounts of

¹ Lord Berkeley, *Phil. Mag.*, 24, 664 (1912).

² Bridgman has shown that the diminutions of volume of mercury caused by 1000 kg./cm². pressure at 0° and 22° are, respectively, 0.374 and 0.391% (*Proc. Am. Acad.*, 47, 380 (1911)). Hence the compressibility of mercury changes nearly 0.2% of its value per degree centigrade. Taking the compressibility of mercury at 20° over the range 100–500 megabars as 0.00000396 (Richards and Bartlett, *This Journal*, 37, 477 (1915)), its value at 25° must then be 0.00000400.

mercury actually added in the 4 cases, we obtain the figures 0.2035, 0.2043, 0.2048 and 0.2028: The departure of these figures from the mean 0.2039 indicates the actual error of experimentation. It is seen, then, that one can fairly count on the errors not exceeding one mg. of mercury in any given case, corresponding to a volume of less than 0.0001 cc.

No. of expt	Wt. H ₂ O G.	Wt. Indium G	Successive totals of added mercury Mg.	Successive pressures. Megabars	(w or w') Wt of added Hg from 100 to 500 megabars G	Mean compress- ibility of indium × 10 ⁶ .
			0	60.0		
1.	0.9463	0	29.8	113.9	0.2082	
			76.2	119.6		
			127.3	296.3		2.70
			230.0	499.2		
			0	111.5		
2.	0.9247	6.693	96.8	306.3	0.1973	
			198.1	514.7		
			0	101.6		
3.	0.9309	0	99.5	289.3	0.2058	
			204.2	498.5		2.57
			0	114.7		
4.	0.9295	6.690	99.1	309.0	0.1984	
			187.7	493.1		
			0	87.4		
5.	0.9235	0	100.4	276.1	0.2049	
			208.5	491.3		
			0	84.4		2.73
6.	0.9222	6.690	11.9	106.7		
			110.4	300.3	0.1988	
			215.3	519.0		
			0	87.7		
7.	1.0025	0	149.5	315.4	0.2212	
			232.0	506.8		
			0	99.0		2.75
8.	0.9963	6.238	120.2	317.9	0.2141	
			215.2	501.2		
Total average mean compressibility of indium.						2.69

The actual error of any given pair of trials was doubtless even less than this, since especial care was taken to have each determination in a pair made under precisely similar conditions.

We are glad to express our indebtedness to the Carnegie Institution of Washington for financial assistance in this research.

Summary.

1. A modification of the usual piezometer was employed which allowed of accurate determination with very small amounts of solid material.

2. A convenient graphic method of extrapolating (for short distances) certain types of curves was employed.

FREDERICK G. KEYES.

3. The compressibility of indium at 25° over the range 100–500 megabars was found to be 0.0000027, or about $\frac{2}{3}$, that of mercury.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 117.]

ON THE ESTABLISHING OF THE ABSOLUTE TEMPERATURE SCALE.

By FREDERICK G. KEYES.

Received September 29, 1919

A new equation of state was published¹ by the author, in 1917, based on an attempt to use the atom essentially as conceived by Bohr. The simplest form of the equation is that which would be valid for a system of one type of molecules, which is to say, substantially completely unasociated. The equation is as follows where p is the pressure, v the volume and T the temperature on the absolute scale,

$$p = \frac{RT}{v - \delta} - \frac{A}{(v - l)^2}.$$

In this equation δ is a function of the volume for polyatomic molecules and a constant for monatomic gases. Since, however, δ is equal to $\beta e^{-\alpha/v}$, where β and α are constants, the term δ reduces to β at large volumes.

In the paper referred to above the fundamental difference in the constant δ corresponding to van der Waals' (b) constant was predicted for a monatomic system as compared to a diatomic system of molecules. Argon and atmospheric nitrogen were chosen as examples, to test the prediction derived from the physical basis used to obtain the equation, the data for the former gas being due to Onnes. For the latter gas, data due to Amagat was employed. The constant δ was found to be constant in the case of argon and a function of the volume for atmospheric nitrogen. The agreement of the calculated pressures with the pressures recorded by Amagat for atmospheric nitrogen at temperatures from 0° to 200° is so close even up to 1000 atm. that it is interesting to investigate what comes out of the application of the atmospheric nitrogen equation to the problem of establishing the absolute temperature scale.

The usual mode of computing the corrections which a gas temperature scale requires has involved the use of Joule-Thomson data for the particular gas used. E. Buckingham reviewing the available data in 1907 completed an investigation which leaves nothing to be desired as regards completeness and skill. Recently more precise data has been supplied by L. G. Hoxton, but the temperature range has not yet been extended sufficiently to affect materially the conclusions reached by Buckingham.

¹ *Proc. Nat. Acad. Sci.*, 3, 323 (1917).

Corrections for the different gas thermometers as well as the position of the ice point on the absolute scale have also been computed by Berthelot by means of an empirical relation involving the critical constants used to modify the equation of van der Waals. The results arrived at are not in general very different from the conclusions reached by Buckingham in his investigation.

TABLE I.

Atmospheric Nitrogen Equation of State.*

Pressures in Atmospheres of 760 mm. Volumes in cc. per g.

V.	$t = 0^\circ$	16.03°	99.45°	199.5°	
5.354	149.8	161.8	225.4	299.7	Computed pressure by equation
	150.0	162.0	225.0	299.0	Observed pressure by Amagat
4.150	199.8	217.2	306.6	414.0	Computed pressure by equation
	200.0	217.0	307.0	414.0	Observed pressure by Amagat
3.46	250.4	273.1	390.3	531.3	Computed pressure by equation
	250.0	273.0	392.0	530.0	Observed pressure by Amagat
3.024	299.7	327.6	472.4	646.4	Computed pressure by equation
	300.0	328.0	474.0	644.0	Observed pressure by Amagat
2.729	347.7	381.1	552.9	759.5	Computed pressure by equation
	350.0	383.0	556.0	758.0	Observed pressure by Amagat
2.511	396.0	434.4	632.8	870.8	Computed pressure by equation
	400.0	439.0	637.0	869.0	Observed pressure by Amagat

* The volume of one gram at one atm. as determined by experiment is 795.62 cc. This volume substituted in the equation of state gives 1.0004 atm. instead of 1.0000 atm.

$$p = \frac{2.9138}{v - \delta} \quad T = \frac{1587.2}{(v - 0.007)^2}$$

$$\log_{10} \delta = 0.2200 - \frac{0.284}{V} \quad \text{or} \quad \delta = 1.66 e^{-\frac{0.653}{V}}$$

Apparent mol. atmospheric nitrogen assumed 28.163

1.66% argon by weight

98.34% nitrogen by weight

The constants of the equation used for atmospheric nitrogen were, as has been stated, taken from the data of Amagat between about 150 atm. and 1000 atm. at 0° to 200° . The differences between the computed and observed pressures, first and second horizontal rows, respectively, Table I, it will be observed nowhere exceed the probable error of measurement. It is evident that the mathematical form of the equation for this gaseous system is such that at constant volume the pressure is a linear function of the temperature.

The data for all the gases for which Amagat gives data may in fact be accurately represented by the same mathematical form of equation and since at these comparatively high pressures the isometrics appear to be linear with so great a degree of approximation, at the low pressures employed in gas thermometry the exactness of the linear increase of pressure with tem-

perature must be very great. It follows from this, that the constant volume gas thermometer reads directly on the absolute temperature scale and therefore requires no correction. This was the conclusion reached by Regnault from a comparison of constant volume thermometers filled with different gases and employed at different initial or ice-point pressures. The doubt regarding the matter appears to rest largely upon certain measurements of the mean constant volume expansion coefficients at intervals between 0° and 100° determined by Chappuis. These coefficients showed a variation greater than the assumed errors of observation, but I have always been puzzled to understand how Chappuis picked off any desired interval with sufficient exactness between the freezing and boiling points of water. It was actually done by means of mercury thermometers, but a very minute error in locating the absolute temperature within the interval 0° to 100° would easily account for the variation of the coefficients found. The most exact method of deciding whether any given constant volume gas thermometer requires correction to reduce its readings to the absolute scale would certainly appear to resolve itself into determining whether the isometrics at high pressures are linear functions of the temperature or not.

Of course this procedure, it may be objected, assumes that a constant volume of gas can be carried from one point on the absolute scale to successive temperatures also on the absolute scale. The consideration, however, to be emphasized is, that if pressures from 100 to 1000 atm. for constant volumes of gas increase in a substantially linear manner with temperature as given by the low pressure constant volume gas thermometer; then at the low pressures always employed in constant volume gas thermometry the straight line isometrics must be sufficiently exact to warrant the assumption that the thermometer readings really lie on the absolute scale.

Besides atmospheric nitrogen, air, oxygen, hydrogen and helium isometrics appear to show so exactly a linear increase of pressure with temperature increase at high pressure that the further consequences of assuming that the indications of the constant volume gas thermometer readings employing the latter gases also lie on the absolute scale is perhaps worth presenting.¹

¹ In considering the data given by the various investigators who have occupied themselves with gas thermometers, it is difficult to avoid the conclusion that adsorption of the gas on the thermometer walls may have had much to do with a great many of the discordant results presented in the literature. Humoropoulos, for example, repeatedly obtained too high a nitrogen expansion coefficient until he had heated the quartz thermometer bulb to a high temperature in vacuum several times. It is because of the adsorptive effect of gases in gas thermometry that metal thermometer bulbs offer a great advantage as compared with glass, porcelain or even quartz,

TABLE II.
Constant Volume Gas Thermometer.

Observer.	ρ_a . Nitrogen.	α at 0° to 100° . Nitrogen.	T_a calculated.
Chappuis	528.8	3.66811 Pt	273.094
Chappuis	534.3	3.66846 Pt	273.072
Chappuis	793.5	3.67180 Pt	273.057
Chappuis	995.9	3.67466 Pt	273.018
Day and Clement	314.0	3.6650 Pt-Ir	273.133
Day and Clement	550.0	3.6680 Pt-Ir	273.128
Day and Clement	744.0	3.670 Pt-Ir	273.147
Day and Clement	985.0	3.673 Pt-Ir	273.139
Holborn and Henning	620.6	3.6684 Quartz	273.153
Holborn and Henning	631.3	3.6705-59 ^{III} Glass	273.007
Holborn and Henning	621.3	3.6702-59 ^{III} Glass	273.022
Hydrogen			
Onnes and Bondiu	1100.0	3.6627 Glass	273.148
Chappuis	1000.0	3.66256 Pt	273.147
Travers, Senter and Jaquero	700.0	3.6626 Quartz	273.110
Holborn and Henning	623.0	3.6625-59 ^{III} Glass	273.112
Helium			
Holborn and Henning	614.0	3.6618-59 ^{III} Glass	273.113
Constant Pressure Gas Thermometer.			
Chappuis	100.0	3.6722 Pt	273.05
Chappuis	1387.0	3.676 Pt	273.01
Regnault	760.0	3.667 Glass	273.05
Eumorfopoulos	395.0	3.6656 Quartz	273.130
Eumorfopoulos	415.0	3.66587 Quartz	273.126
Eumorfopoulos	792.0	3.67005 Quartz	273.123
Eumorfopoulos	784.0	3.67019 Quartz	273.106
Eumorfopoulos	757.0	3.66991 Quartz	273.106
Hydrogen			
Chappuis	1000.0	3.6600	273.115
Richards, Marks and Witkowski	760.0	3.6610	273.067

Assuming then that the readings of the constant volume nitrogen thermometer lie on the absolute scale, the corrections which would follow from applying the equation of state given for atmospheric nitrogen to the constant pressure thermometer will be given and also the position of the ice point on the absolute temperature scale as computed by means of the equations for the several other gases, using for this purpose the mean constant volume and constant pressure 0° to 100° expansion coefficients.

The correction equation, details of which are to be given in a later more complete paper, for the nitrogen constant pressure thermometer, is

$$t_a - t = 5.74 \times 10^{-3} t - 3.31 \times 10^{-6} \frac{(2 + t)}{(1 + t)} t,$$

where the pressure is 1000 mm. and t_a the reading on the absolute scale, t that of the gas scale and ϵ has a value of 0.00366. The mean coefficient equation for ϵ_p^a for nitrogen between 0° and 100° is, where $\epsilon = 1/273.135 = 0.0036612$

$$\epsilon_p^a = \epsilon + 1.098 \times 10^{-8} p - 4.24 \times 10^{-14} p^2,$$

where the pressure is expressed in mm.

The equation for ϵ_p^a , the coefficient¹ for the constant volume nitrogen thermometer, follows very simply from the nitrogen equation of state and is $\epsilon_p^a = 0.0036612 + 1.0207 \times 10^{-8} p_0$, where p_0 is measured in mm

Table II gives the ice point on the absolute scale as calculated for each of the kinds of expansion coefficient. The constant volume data of Day and Clement are by far the most reliable and give the mean value 273.137. The work of Eumorfopoulos, wherein a quartz bulb was used, is quite reliable and gives the mean 273.118. If these two values are averaged with the Onnes hydrogen, and the Holborn and Henning hydrogen and helium values, the mean comes out 273.126. The coefficients obtained by Day and Clement, however, for the measurement of which a platinum iridium bulb was employed whose coefficient of expansion was carefully investigated, would appear most reliable. The mean value 273.137 for the ice-point is therefore believed to be nearly correct. The number 273.14 may be accepted. The number decided upon by Buckingham was 273.13.

TABLE III.
Sulfur Boiling Point.

Constant volume thermometer.		Constant pressure thermometer.		
Observer	Nitrogen gas thermometer	Observer	Nitrogen gas thermometer.	Abs cent temp
		Eumorfopoulos	444.392 $p_0 = 395$	+0.197 444.59
Chappuis and Harker	444.70 Coef. Exp. of porcelain uncertain	Eumorfopoulos	444.356 $p_0 = 415$	+0.208 444.56
Reichsanstalt, Wiebe & Bötcher	444.50	Eumorfopoulos	444.125 $p_0 = 757$	+0.378 444.50
Holborn	444.55	Eumorfopoulos	444.140 $p_0 = 784$	+0.392 444.53
Extrap. Pt. Res.		Eumorfopoulos	444.125 $p_0 = 892$	+0.396 444.52
Holborn and Henning	444.51			
Mean, last 3	444.52	Eumorfopoulos	Mean	444.54

The sulfur boiling-point temperature has not shown agreement as measured on the constant volume and constant pressure gas thermom-

¹ The superscript a in ϵ_p^a refers to the actual coefficient at constant pressure, denoted by the subscript as distinguished from the ideal coefficient ϵ . The ϵ_p^a refers similarly to the expansion coefficient at constant volume of an actual gas.

eters. The constant pressure thermometer work at this fixed point suffered from the fact that a bulb of suitable material has only recently been employed. In the paper by Eumorfopoulos¹ the sulfur point was measured at several different pressures by means of a quartz bulb Callendar gas thermometer. With the corrections appropriate to the scale these various temperatures of boiling sulfur have been corrected by means of the correction equation given above. The corrected values appear in Table III, together with the values of the sulfur boiling point obtained recently with the constant volume thermometer. A small table (Table IV) of the corrections computed from 0° to 1000° is also given and values obtained by E. Buckingham through the Joule-Thompson numbers are listed for comparison.

TABLE IV.

Constant Pressure Nitrogen Thermometer.

Corrections computed by the equation of state compared with those computed from Joule-Thompson coefficients. $p = 1000$ mm.

T .	$(t_g - t)$ Computed equation of state	$(t_g - t)$. E. Buckingham.
20	-0.0123	-0.0137
40	-0.0184	-0.0203
60	-0.0176	-0.0198
80	-0.0009	-0.0129
200	+0.103	+0.103
444	+0.500	+0.502
600	+0.84	+0.827
800	+1.28	+1.262
1000	+1.72	+1.706

Attention is called to the close agreement of the scale corrections obtained by such diverse methods. Of course if the linear increase of the pressure with temperature is as exact as it appears to be in the case of nitrogen and argon, hydrogen and helium at higher temperatures, for the low pressures employed in thermometry the constant volume thermometer would certainly need no correction.

The sulfur boiling point mean corrected to the absolute scale as indicated is 444.54 for the constant pressure gas thermometer whereas the constant volume thermometer mean of the recent work is 444.52.

CAMBRIDGE, MASS.

¹ *Proc. Roy. Soc. (London)*, 90A, 189 (1914).

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

SOME CHARACTERISTICS OF THE GOUY THERMOREGULATOR.

By T. S. SLIGH, JR.

Received October 2, 1919

Gouy¹ has described briefly a modification of the usual form of thermoregulator which produced a considerable improvement in the temperature regulation of a 100-liter water bath. Barnes² also made favorable comment on this device as applied to his work on the heat capacity of water.

While seeking means of overcoming some of the difficulties encountered in the use of the thermo-regulator for precise work, the author in 1918 arrived at the use of an oscillating contact as one solution. Later, reference to Gouy's description of this device was found, but since no direct comparison was there drawn between the fixed and oscillating contact type of thermoregulator and no mathematical expression defining the operation of the Gouy modification had been published and since, furthermore, the device appears not to have received the attention and use which its excellence and simplicity warrants, it was thought that this discussion would be of general interest.

The usual type of thermoregulator used in laboratories for precise regulation of temperatures consists of a bulb filled with an expansive liquid and connected to a glass U-tube which is partially filled with mercury. The variation in position of the mercury meniscus is caused to vary the energy input to the bath by throttling the supply of gas to a burner, by changing the electrical energy supply to a heating coil, etc.

Fig. 1 shows the U-tube and electrical connections arranged for electrical control of temperatures. In the usual form of regulator the platinum wire A is fixed in position. A rise in temperature of the regulator bulb causes the meniscus B to make contact with A whereupon current flows through the relay circuits opening a contact at D, thus introducing an additional resistance R_1 in the heating circuit, or opening this circuit entirely.

Gouy's modification consists in imparting to the platinum wire A an oscillating motion of 20 seconds period along the axis of the tube. His arrangement of electrical circuits was such that the entire heating current was interrupted when separations between the points A — B occurred. In this manner energy was periodically supplied to the bath during that part of the cycle of motion of the platinum wire during which A and B were not in contact. An increase in the temperature of the thermoregulator bulb results in a rising of the meniscus B which causes a decrease in the length of time during which energy is periodically supplied

¹ *J. Physique*, 6, 479 (1897)

² *Phil. Trans. Roy. Soc.*, 190, 208 (1902)

to the bath, thus tending to stabilize the bath temperature. Gouy reports that the use of this device greatly reduced the errors due to the compressibility of the thermostatic fluid and to the distortion of the mercury meniscus as it moved up or down. He also states that regulation to within 0.0002° as measured by an extremely sensitive alcohol thermometer was maintained over periods of some hours and that the oscillation of mean bath temperature produced by the variations in heating was imperceptible.

Fig. 1 shows the oscillating device used by the author of this paper. A platinum wire A fitted to a guide plug E which fits the capillary tube loosely is given a periodic oscillating motion along the axis of the capillary tube by means of the cam and spring mechanism shown. The range of this motion may be conveniently 0.1 cm. and the period of the motion

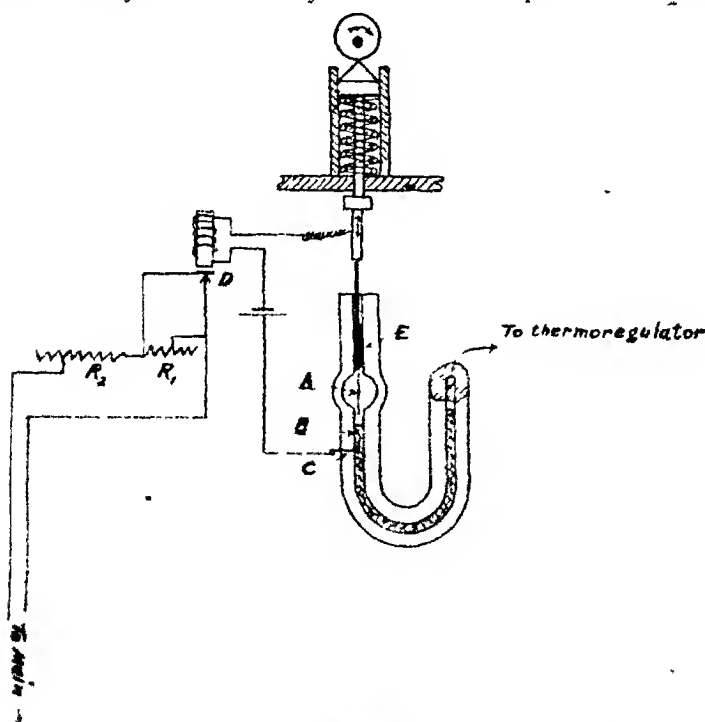


Fig. 1.

one second. This period may be varied over a wide range without affecting the regulation perceptibly; the lower limit being set by the disturbance of the mercury surface at extremely short periods and the upper limit by the time lag of the thermoregulator with respect to the heater. This time lag may be defined as the number of seconds which would elapse

between the time when a certain quantity of heat, q , has been generated in the heater; the rate of heating being constant and continuous; and the time when the mercury meniscus of the thermoregulator has assumed a position corresponding to this quantity of heat.

The extent to which periodic variations of bath temperature due to operation of the regulator are reduced may best be illustrated by an experimental comparison between the usual or fixed contact type of thermoregulator and the Gouy modification or oscillating contact type, since this is not a matter which lends itself readily to analytical treatment.

The thermoregulator as illustrated in Fig. 1 was used as a fixed contact type to regulate the temperature of a water bath. By means of a very close adjustment of the external resistances, it was found possible to obtain a regulation where the up and down variation of bath temperature produced by the "on" and "off" action of the regulator was about 0.001-0.002 of a degree centigrade. This adjustment was not, however, practical since very slight changes in external conditions would cause the regulator to lose control. A practical adjustment, *i. e.*, one which would maintain control over a period of several hours under average laboratory conditions, was found to give a periodic variation of about 0.005°. The platinum wire was then given a reciprocating motion along the axis of the capillary with a periodicity of one second and it was found that the variation of bath temperature with operation of the regulator as indicated by a calorimetric platinum resistance thermometer was less than 0.0001°, even when the adjustment of the external resistances was such as would give a variation of approximately 0.01° with fixed contact. The above mentioned resistance thermometer was used with a galvanometer having a period of about 5 seconds. It is, therefore, probable that short period fluctuations of temperature considerably larger than the amount indicated (0.0001°) actually occurred. However, temperature fluctuations which are of too small period and amplitude to affect a calorimetric resistance thermometer would probably have a negligible effect in any but the most extreme cases. The periodicity of the motion was varied between 0.3 second and 3 seconds without observable effect upon the regulation. The time lag of the bath used was about 10 seconds. It is not to be understood that the operation of the regulation with fixed contact was the best obtainable with this type of regulator. In fact the mercury surface was known to be in bad condition, however, since the change to the oscillating contact was the only variation introduced, the comparison may be considered typical.

An analytical consideration of the operation of the two types of regulators (see appendix) results in the following characteristic equations. Symbols have the meanings indicated in appendix.

For fixed contact thermoregulator, the periodic change in temperature as the regulator operates is

$$\Delta\theta_p = \frac{tW}{M} + \Delta\theta'. \quad (2)^1$$

The changes in mean bath temperature, $\Delta\theta_m$, produced by changes in thermal head, $\Delta\phi$, and by changes in maximum electrical input controlled by regulator, ΔW , is

$$\Delta\theta_m = t/2M \cdot \Delta W + -tK \Delta\phi. \quad (1)$$

The corresponding formulas for the oscillating contact regulator are:

For changes in mean bath temperature, $\Delta\theta_m$, due to changes in thermal head, $\Delta\phi$, and changes in average electrical distribution along the path of the moving contact ΔW ,

$$\Delta\theta_m = \frac{MK\phi_1}{\alpha W_1 W_2} \Delta W - \frac{MK\Delta\phi}{\alpha W_2}. \quad (5)$$

The expression for the variation in bath temperature as the regulator operates is not derived but experiment shows this variation to be small. The numerical calculations in the appendix indicate the advantages in regulation which may be gained by the use of an oscillating contact regulator. The principal advantages of this type of regulator over the fixed contact are:

1. A large range of available energy input and consequently a large range of regulation may be obtained without a sacrifice of closeness of regulation.

2. A bath temperature is obtained in which the periodic variations about the mean due to operation of the regulator are very greatly reduced.

3. The variation introduced by variations in the mercury surface due to soiling, sticking, etc., are largely eliminated.

It is clear that the advantages to be secured by the use of the oscillating contact type of regulator are due to the fact that the time at which a given movement of the meniscus may affect the energy input is rendered independent of the physical constants of the bath and dependent only upon the periodicity of the oscillating element of the regulator, and to the provision of a means for applying successive corrections at short time intervals to the value of the energy input instead of corrections at such longer time intervals as will permit of wider excursions of bath temperature above and below its mean value.

The conditions to be fulfilled for successful operation of an oscillating contact thermoregulator are:

1. The periodicity of the oscillation should be small in comparison

¹ Equation numbers are taken from the order in which they appear in the appendix.

with the lag of the bath, say $1/4$ of this value, but not so small as to produce sustained waves on the mercury surface. There seems to be no advantage in reducing the period beyond that necessary to damp the periodic fluctuations in bath temperature sufficiently to render their effects imperceptible.

2. The length of path of the oscillating element should be large in comparison with the movement required to make or break contact with the mercury surface, one mm. seems to be sufficient in most cases.

3. The energy distribution along the path of the oscillating element should be large in order that great range and close regulation may be secured under a wide range of external conditions. The upper limit to this energy distribution is fixed by the fact that the smallest amount of energy which may be supplied during a single cycle should not exceed that which is required during that cycle. Violation of this condition would result in a motion of the meniscus beyond the limits of the stroke of the oscillating element. An upper limit to the energy distribution lower than that indicated above may be imposed by the current carrying capacity of the relay contacts, etc.

It will be seen that the method of energy control exemplified in the oscillating contact thermoregulator can be applied readily to a wide variety of forms of manual or automatic control of various physical quantities.

Summary.

The paper describes a modification of the usual type of thermoregulator in which the fixed contact element is replaced by an oscillating contact element and shows that such a regulator will reduce the periodic variation of the bath temperature and the erratic variations due to variations of the mercury surface to a fraction of the values to be obtained with the usual form of thermoregulator. A periodic variation in bath temperature of less than 0.0001° as indicated by a temperature indicator having a natural period of about five seconds is easily obtained.

In addition, by use of an oscillating contact regulator, variations of mean bath temperature due to variations in external conditions are reduced below the values usually obtained.

Characteristic equations are derived for both the fixed and oscillating contact type of thermoregulator and these equations together with experimental evidence have been used to draw a comparison between the two types of regulator.

Appendix.

The effects of variations in external conditions upon the temperature of the bath will be considered, it being understood that in this discussion "temperature of bath" means specifically the temperature of that portion of the bath which is in immediate contact with the thermoregulator

The relation between the temperature of this portion of the bath and the temperature of the bath as a whole is of course dependent upon the degree of mixing of the bath fluid, the relative positions of the heater and the thermoregulator and the degree of thermal contact between the bath, heater, thermoregulator and cooling surfaces. It is also assumed that the lag of the bath as a whole with respect to the heater is less than the lag of the thermoregulator with respect to the heater. If this were not the case, *i. e.*, if the thermoregulator were very closely coupled thermally with the heater, the effective heat capacity of the bath defining the operation of the thermoregulator would be less than the real heat capacity of the bath. Effects of exposed stem volume are neglected.

Fixed contact regulator:

Let K = cooling constant of bath, deg /sec deg.

ϕ = the portion of the thermal head of the bath, *i. e.*, difference in temperature between the exposed portion of the bath and its surroundings, which is compensated by the thermoregulator. This does not include the portion of the thermal head which is compensated by the fixed heating. ϕ is considered positive when the bath loses heat to the surroundings.

$R_c = K\phi$ = cooling rate, deg /sec.

R_h = rate of temperature rise of bath when energy is being supplied, deg /sec.

Z = average temperature at which "make" and "break" occurs.

$\Delta\theta'$ = contact lag; the change in temperature required to change the contact of the thermoregulator from "make" to "break." This quantity has been found to vary rather erratically by as much as 50% under ordinary conditions.

$\Delta\theta_p$ = total change in temperature during one cycle of "make" and "break." Amplitude of the periodic oscillations of temperature

θ = instantaneous temperature of bath.

θ_m = mean temperature of bath.

W = maximum electrical input supplied by regulator, watts; not average input.

M = heat capacity of bath, joules/deg.

t = time lag of thermoregulator, seconds. This quantity is defined as the number of seconds which would elapse between the time when the total energy input to the bath has reached a value corresponding to a given meniscus position and the time when the meniscus assumes this position, supposing the rate of energy input to be approximately constant.

Now, $R_c = K\phi$ and $R_h = W/M - R_c = W/M - K\phi$.

Then approximately

$$\theta_m = Z + t/2 (R_h - R_c) = Z + t/2 (W/M - 2K\phi).$$

Expressing finite changes, θ_m , in terms of changes in ϕ and W we have

$$\Delta\theta_m = \frac{t}{2M} \Delta W - tK \Delta\phi, \quad (1)$$

which is the characteristic equation for the fixed contact thermoregulator.

The magnitude of the periodic change in bath temperature as the thermoregulator operates is

$$\Delta\theta_p = tR_c + tRh + \Delta\theta' = \frac{tW}{M} + \Delta\theta'. \quad (2)$$

Oscillating contact regulator.

Let α = sensitivity of thermoregulator, the movement of meniscus in cm. per degree change in bath temperature

θ = instantaneous bath temperature.

θ_m = mean bath temperature

ϕ = thermal head as defined for fixed contact regulator.

y = length of path of oscillating contact in centimeters over which energy is being delivered to the bath

W = electrical energy distribution along the path of the oscillating element expressed in watts/cm., $\pm \epsilon$, a change of 0.1 cm. in position of the meniscus would change the average power input by $W/10$ watts

For equilibrium conditions it is evident that we must have the condition

$$y = \frac{MK\phi}{H}.$$

Expressing finite changes in y in terms of finite changes in ϕ and W we obtain,

$$\Delta y = \frac{MK\Delta\phi}{H_2} - \frac{MK\phi_1\Delta W}{H_1W_2}, \quad (3)$$

where the subscripts 1 and 2 denote values before and after the change considered has taken place:

Now by definition of α ,

$$\Delta y = -\alpha\Delta\theta_m. \quad (4)$$

Substituting this value for Δy in Equation 3 we have

$$\Delta\theta_m = \frac{MK\phi_1}{\alpha W_1 W_2} \Delta W - \frac{MK\Delta\phi}{\alpha W_2}, \quad (5)$$

which is the characteristic expression for the oscillating contact thermoregulator.

As an experimental verification of the above equations observations were taken of the action of a thermoregulator operating first as a fixed and then as an oscillating contact type. The bath used was the water jacket of the calorimeter described in the Bureau of Standards, *Scientific Paper* 231.

The time lag of the thermoregulator with respect to the heater was obtained as follows: The energy input to the heater was changed from a value which gave a zero temperature rate to one which would give a fairly large rate and reckoning from the time at which this change was made data for the time-displacement curve of the mercury meniscus of the thermoregulator were taken. This curve was plotted and the constant displacement rate which was attained after about thirty seconds was projected back to cut the time axis. This intercept gave a single de-

termination of the time lag of the bath. The final value was the mean of a number of such observations.

The other constants of the bath and regulator were determined in the usual manner and found to be as follows:

Heat capacity of bath, M , = 80,000 joules/deg.

Cooling constant of bath, K , = 0.000053 deg./sec./deg.

Time lag, t , = 8.4 seconds.

Sensitivity of regulator, α = 2.65 cm./deg.

Temperature change for "make" to "break" $\Delta\theta' = 0.0025^\circ \pm 0.0005$.

Length of stroke of oscillating contact = 0.103 cm.

Period of oscillating contact = 1.7 seconds.

In order to secure changes in θ_m which could be observed with the desired accuracy it was necessary to change the working conditions of the thermoregulator very widely. It is to be understood that changes of this order of magnitude would seldom be met with in practice.

Observations were taken and calculations made as indicated in the tables below.

Fixed Contact Regulator.

$$\Delta\theta_m = t/2M \Delta W - tK \Delta\phi.$$

$$\Delta\theta_p = tH'M + \Delta\theta'.$$

No.	W watts.	ΔW watts.	ϕ Deg.	$\Delta\phi$ Deg.	$\Delta\theta_p$ obs Deg.	$\Delta\theta_p$ calc Deg.	$\Delta\theta_m$ obs Deg.	$\Delta\theta_m$ calc. Deg.
1.....	50	+ 50	--	0	0 0070	0 0078	+0 0027	0.0026
2.....	100	+ 50	--	0	0 0120	0 0130	+0 0025	+0 0026
3.....	150	--100	--	0	0 0170	0 0180	--0 0050	--0 0052
4.....	50	-- 20	--	0	0.0073	0 0078	--0 0010	--0.0011
5.....	120	-- 40	19	-10.5	0 0150	0 0150	--0 00021	--0.0023
6.....	70	+ 50	16	+3 0	0 0085	0 0076	+0 0033	+0.0029
7.....	125	-- 37	19	--9.8	0.0170	0 0160	--0 0020	--0.0021

Oscillating Contact Regulator.

$$\Delta\theta_m = \frac{MK\phi_1}{\alpha W_1 W_2} \Delta H' - \frac{MK}{\alpha W_2} \Delta\phi$$

No.	W_1 watts/cm.	W_2 watts/cm.	ΔW watts/cm.	ϕ Deg.	$\Delta\phi$ Deg.	$\Delta\theta_m$ obs. Deg.	$\Delta\theta_m$ calc. Deg.
1.....	680	1160	480	10.0	0	+0.0096	0.0098
2.....	775	1450	675	10.0	0	+0.0095	0.0096
3.....	970	1160	190	18.5	0	+0.0050	0.0050
4.....	1160	1160	0	10.0	--2.4	0.0037	0.0033
5.....	675	675	0	10.0	--2.0	0.0043	0.0048
6.....	970	970	0	18.5	--10.0	0.0170	0.0165
7.....	1160	1160	0	18.5	--7.7	0.0110	0.0106

The agreement between observed and calculated values seems good in view of the magnitudes and nature of the quantities observed.

The apparatus described above has constants which are more favorable to the fixed than to the oscillating contact type of thermoregulator, furthermore, it is hardly typical in that the heat capacity is

and the time lag smaller than is usual. Constants which are more nearly representative of the average case will be assumed and the variation in θ_m with varying working conditions will be calculated.

$M = 20,000$ joules/deg.

$\phi = 5^\circ \text{ C.}$

$\alpha = 20 \text{ cm./deg. (270 cc. bulb, 1 mm. capillary).}$

$K = 0.0001 \text{ deg./sec./deg.}$

$t = 15 \text{ seconds.}$

$W = 1000 \text{ watts/cm. for oscillating contact}$

$W = 10 \text{ watts for fixed contact.}$

$\Delta\theta' = 0.0004 \text{ deg.}$

Assuming a change of 1° in ϕ . For fixed contact, from Equation 1

$$\Delta\theta_m = 15 \times 0.0001 \times 1 = 0.0015^\circ.$$

For oscillating contact, from Equation 5

$$\Delta\theta_m = \frac{20,000 \times 0.0001 \times 1}{20 \times 1,000} = 0.0001^\circ.$$

The amplitude of the periodic oscillation of temperature is for the fixed contact thermoregulator, from Equation 2.

$$\Delta\theta_p = \frac{15 \times 8}{20,000} + 0.004 = 0.0064^\circ.$$

Experiment has shown that the amplitude of the periodic oscillation of temperature produced by the oscillating contact regulator appears less than 0.0001° .

Assuming the energy input to change by 1% of itself; a change which might be due to a change in the voltage of the supply circuit.

For fixed contact, from Equation 1

$$\Delta\theta_m = \frac{15}{2 \times 20,000} (10 \times 0.01) = 0.000038^\circ.$$

For oscillating contact, from Equation 5

$$\Delta\theta_m = \frac{20,000 \times 0.0001 \times 5}{20 \times 1000 \times 990} \times (1000 \times 0.01) = 0.000005^\circ.$$

Hence the effect of small changes in power input would be negligible in either case.

In conclusion, the author wishes to express his appreciation of the very great assistance rendered by Mr. M. S. Van Dusen of the Bureau of Standards in the preparation and verification of this discussion.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF YALE UNIVERSITY AND THE
RUSSELL SAGE LABORATORY OF THE RENNSÉLAIRE POLYTECHNIC INSTITUTE.]

EQUILIBRIUM IN THE SYSTEM AMMONIA-AMMONIUM THIOCYANATE.¹

By H. W. FOOTE AND M. A. HUNTER.

Received October 30, 1919

It recently became desirable to find absorbents other than water for free ammonia and in this connection the system of ammonia and ammonium thiocyanate has been investigated.

When dry ammonia gas is passed over dry ammonium thiocyanate at room temperature, deliquescence takes place and a clear, nearly colorless solution of the salt and ammonia results. This fact was first mentioned in the literature by Bradley and Alexander,² who determined the solubility of the salt in the liquid over a wide range of temperature and the composition of some of the solid phases.

Our work has been concerned chiefly with the vapor pressure of the liquid phase, but we have also determined the solubility of ammonium thiocyanate in the liquid over a limited range of temperature, and the specific conductance of several solutions at 0°.

Vapor Pressure.

At a given temperature, the vapor pressure of a solution composed of ammonium thiocyanate and ammonia is a function of its composition, varying between the value for the solution saturated with thiocyanate on the one hand and that of liquid ammonia on the other. We have determined vapor pressures at 5 temperatures from 0° to 40° between the limits of the saturated solution and the liquid having a vapor pressure of one atmosphere; and we have also determined the vapor pressure of saturated solutions alone at a number of very low temperatures.

Vapor Pressures from 0° to 40°.

The method used for determining vapor pressures between 0° and 40° consisted in passing pure ammonia gas at a known pressure through a known weight of thiocyanate until no further change in weight occurred. In this way the composition of the liquid corresponding to a known pressure of ammonia was found instead of the more usual method of determining the vapor pressure of a liquid having a known composition. The method is exceedingly simple and gave consistent results.

Dry ammonia was obtained by warming a strong aqueous solution and passing the gas through two towers, the first containing quicklime

¹ A part of this work was carried out in 1911 by one of us and the rest more recently by both at the request of the Division of Chemistry of the National Research Council. The authors are indebted to Dr. John Johnston for some valuable suggestions regarding the work.

² THIS JOURNAL 24, 12 (1900).

and the second fused caustic potash in sticks. The ammonium thiocyanate used was a C. P. product which we recrystallized and dried.

For the determinations, a weighed amount of the salt was placed in an absorption U-tube provided with a glass valve to prevent spattering. The temperature was kept constant by placing the tube in a suitable tank, and when necessary, the ammonia, before entering the U-tube, first passed through a coil immersed in the tank to insure its having the right temperature. For determinations at atmospheric pressure, the excess of ammonia gas passed directly into the atmosphere after leaving the U-tube; for pressures below atmospheric, a tube led from the U-tube into a large bottle in which a constant diminished pressure was maintained. The diminished pressure was produced by a water pump; it was kept constant by admitting air to the bottle after passing through a column of mercury, the height of which could be varied. At low pressures, it was found better to use two mercury tubes in series, each cutting down the pressure by half. This prevented the mercury from spattering too violently. The pressure never varied over a millimeter in a determination. A manometer connected with the bottle gave the pressure readings. Equilibrium between the gas and liquid usually was complete in about 20 minutes. A series of determinations at varying pressures could be carried out with one sample of thiocyanate. The vapor pressure of the saturated solution was obtained either by extrapolation (at 0°) or experimentally by reducing the pressure until crystals of thiocyanate just began to appear and then increasing it slightly until they just dissolved. This also gave the composition of the saturated solution. There is a small error in the results due to the fact that ammonia vapor partly displaces air when the liquid in the U-tube is weighed. In the most unfavorable case, this error only amounted to about 0.1% in the composition of the liquid.

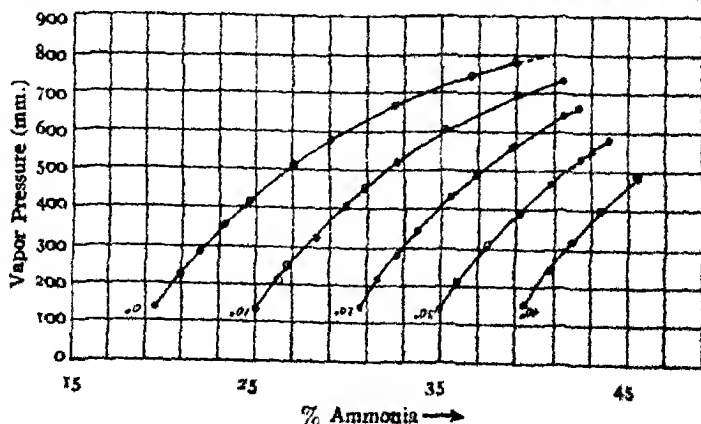


Fig. 1.

The results which were obtained are given below. The values at the highest (atmospheric) pressure are in every case the average of two closely agreeing duplicates. By "per cent. of ammonia" is meant the weight of it in 100 weights of solution. The values in the fourth column at each temperature show the percentage of the vapor pressure of pure ammonia exerted by the vapor of each solution. They are discussed later. The vapor pressures of pure ammonia, P_{NH_3} , at each temperature, are taken from Keyes.¹

$T = 0^\circ.$ $P_{\text{NH}_3} = 3255 \text{ mm.}$				$T = 10^\circ.$ $P_{\text{NH}_3} = 4656 \text{ mm.}$			
NH ₃ %.	NH ₃ molec. %.	Vapor pressure. <i>p</i>	<i>p</i> / <i>P</i> × 100.	NH ₃ %.	NH ₃ molec. %.	Vapor pressure. <i>p</i>	<i>p</i> / <i>P</i> × 100.
44.48	78.15	762	23.41	38.98	74.04	765	16.43
43.00	77.11	677	20.80	37.71	73.00	688	14.78
42.04	76.41	615	18.89	37.32	72.67	648	13.92
40.77	75.45	551	16.93	35.68	71.25	572	12.28
39.42	74.39	489	15.02	34.17	69.86	496	10.65
36.93	72.33	388	11.92	33.14	68.88	448	9.62
34.98	70.61	323	9.92	31.35	67.09	377	8.10
31.57	67.32	233	7.16	28.79	64.35	295	6.34
27.47	62.84	154	4.73	24.95 ^b	59.74	202	4.34
25.06	59.89	120	3.69	22.51 ^b	56.46	167	3.59
23.3 ^a	...	105	...				

$T = 20^\circ.$ $P_{\text{NH}_3} = 6480 \text{ mm.}$				$T = 30^\circ.$ $P_{\text{NH}_3} = 8808 \text{ mm.}$			
NH ₃ %.	NH ₃ molec. %.	Vapor pressure <i>p</i>	<i>p</i> / <i>P</i> × 100	NH ₃ %.	NH ₃ molec. %.	Vapor pressure <i>p</i>	<i>p</i> / <i>P</i> × 100.
33.39	69.12	756	11.67	29.06	64.65	764	8.67
32.38	68.13	682	10.52	28.18	63.66	685	7.78
31.36	67.10	620	9.57	26.61	61.82	589	6.69
30.26	65.96	560	8.64	24.84	59.61	514	5.84
28.52	64.05	473	7.30	23.18	57.40	437	4.96
27.07	62.36	435	6.40	21.57	55.11	371	4.21
25.13	59.98	340	5.25	20.84	54.03	346	3.93
22.43	56.37	259	4.00	19.99 ^b	52.73	316	3.59
21.64 ^b	55.22	237	3.66				

$T = 40^\circ.$ $P_{\text{NH}_3} = 11722 \text{ mm.}$			
NH ₃ %.	NH ₃ molec. %.	Vapor pressure. <i>p</i>	<i>p</i> / <i>P</i> × 100.
24.62	59.32	748	6.38
23.17	57.38	638	5.61
22.03	55.78	587	5.01
20.56	53.61	503	4.29
18.50 ^b	50.34	411	3.51

^a Extrapolated for the saturated solution.

^b Saturated solution.

The vapor pressures are plotted in Fig. 1

¹ THIS JOURNAL, 40, 24 (1918)

Vapor Pressures at Low Temperatures.

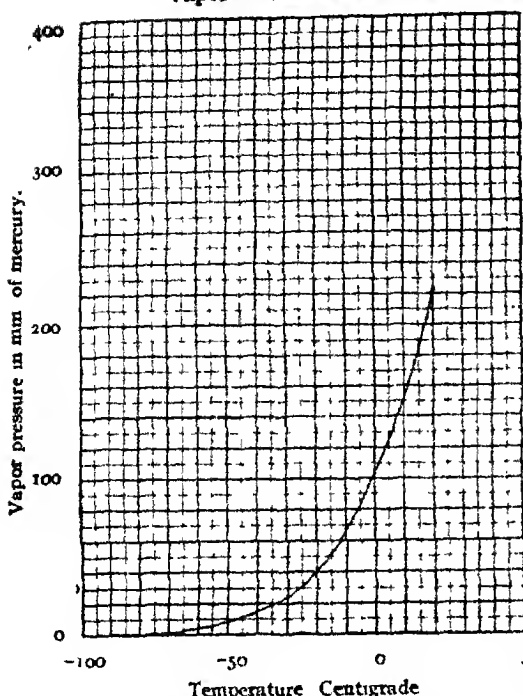


Fig 2 —Vapor-pressure curve Saturated solution of ammonium thiocyanate in ammonia

The vapor pressures of solutions of ammonia saturated with ammonium thiocyanate were determined over the range from -78° to $+20^{\circ}$. A glass bulb containing an excess of the solid salt was connected with a mercury manometer and the pressures were obtained over the range indicated. The bulb was immersed in a bath of solid carbon dioxide and alcohol and measurements of the vapor pressures were made as the bath warmed. The temperature readings were taken with an ordinary toluene thermometer.

The following values were obtained:

Temp. T°	Vapor pressure (mm)
-78	1
-65	4
-50	9
-34	21
-23	34
-20	41
0	107
$+20$	225

These results are plotted in Fig. 2.

Solubility.

Several solubility determinations were made in the course of vapor-pressure determinations as described previously. A number of others were made in the following manner: A weighed quantity of solution, having a known composition, was sealed in a tube with a suitable weighed amount of thiocyanate. The mixture was heated until all dissolved, then cooled rapidly to from -78° to -100° and the mixture was allowed to warm slowly to the temperature of measurement.

bath, the temperature could be determined at which the last of the crystals dissolved. At this temperature, the composition of the contents of the bulb is that of the saturated solution. The following results were obtained. Those marked with an asterisk were obtained during the vapor-pressure determinations.

Temperature T° .	NH_3 %	NH_4CNS %
2.8	23.13	76.87
10.0*	22.51	77.49
20.0*	21.64	78.36
23.3	21.48	78.52
30.0*	19.99	80.01
31.0	19.86	80.14
33.0	19.24	80.76
40.0*	18.50	81.50
49.8	16.67	83.33

Individual results are not without appreciable error but the two methods give results agreeing reasonably. The results have been plotted and a curve drawn through them from which the following results have been taken

Temperature T°	NH_3 %	NH_4CNS %
0	23.3	76.7
10	22.65	77.35
20	21.6	78.4
30	20.15	79.85
40	18.4	81.6
50	16.65	83.35

Bradley and Alexander¹ obtained results noticeably higher in thiocyanate. The two methods which we used in determining solubility gave results agreeing reasonably and we cannot believe they are far from the facts.

Discussion of the Results.

A glance at the results on vapor pressure between 0° and 40° will show that ammonium thiocyanate is exceedingly soluble in ammonia and that the vapor pressure of the latter has been greatly lowered by the dissolved salt. As an illustration, at 20° , the saturated solution contains 78.4% of thiocyanate and the vapor pressure is 237 mm. The vapor pressure of pure ammonia at this temperature is about 6500 mm. This lowering in vapor pressure is abnormally great and not of the same order that would be produced according to Raoult's law, even if the salt were completely dissociated. In the fourth column of the tables, the percentage of the vapor pressure of pure ammonia exerted by the vapor of each solution has been calculated. If Raoult's law held for the solutions, these values should equal the molecular percentages of ammonia in the second column. Depending on the temperature and concentration, the values

¹ *Loc. cit.*

of vapor pressure calculated by Raoult's law are from about 3 to 15 times the values actually found.

In Fig. 3, the percentage values of vapor pressure, $(p/P) \times 100$, taken from the fourth column of the table, have been plotted (for 0° , 20° and 40°) as a function of composition. The values for the two intermediate temperatures are omitted as they tend to confuse the diagram. From

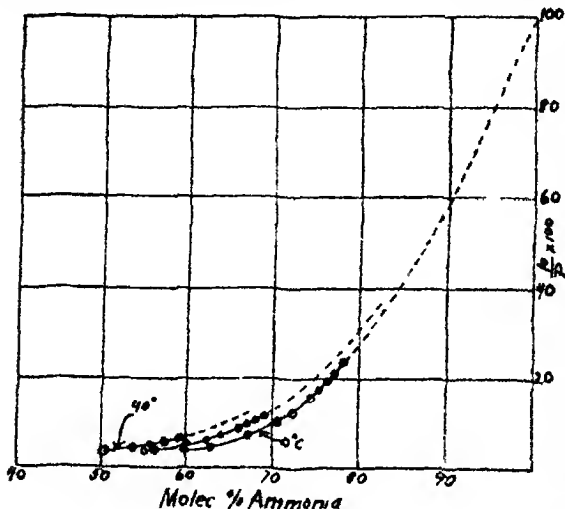


Fig. 3

the form of the curves, especially the one at 0° , it is evidently possible to estimate approximately the values for $(p/P) \times 100$ in more dilute solutions.

Aside from the effect of electrolytic dissociation and possibly the association of liquid ammonia, the abnormal lowering of vapor pressure caused by ammonium thiocyanate is probably

due largely to ammonia addition products in solution. If the deviation from Raoult's law was due entirely to the last mentioned cause, the average composition of the compound in solution could be calculated by Callendar's equation¹

$$\frac{p_0 - p}{p_0} = \frac{n}{N - an + n'}$$

in which p_0 and p represent, respectively, the vapor pressures of pure ammonia and of the solution, n and N the molecules of solute and of solvent, and a the molecules of solvent combined with solute. Taking 3 values at random from our results at 0° , the corresponding values of a are as follows

$\pm \text{NH}_3$ mol. %	a
78 15	3.26
74 39	2.72
62.84	1.64

The values of a increase with increasing concentration of ammonia, which is to be expected, but they are undoubtedly too high as a part of

¹ *Proc. Roy. Soc. Lond.* 166 (1902); *Proc. Roy. Soc. Lond.* 166 (1902).

the abnormal lowering is due to dissociation of the thiocyanate in solution. That dissociation is present, is shown by the high conductance of the solutions. The following results were obtained at 0°:

NH ₄ mol. %	Specific conductance
75.0	0.1979
68.9	0.1640
63.3	0.1395
59.7	0.1246
57.1	0.1110

The solutions contained such a high percentage of thiocyanate that the conductance decreases with increasing concentration of the salt but the values indicate considerable dissociation though the data are not sufficient to calculate the amount.

Association of liquid ammonia, if it exists, like dissociation of the thiocyanate or compound formation in solution, would cause lower vapor pressures than those calculated by Raoult's law since the molecular percentage of ammonia would be less. Calculation shows, however, that to account for the abnormal lowering in the present case, the liquid must be very highly associated and the association must increase as the concentration of ammonia decreases. It does not seem likely, therefore, that association of ammonia plays any considerable part in the abnormal lowering of vapor pressure in the present case.

The lowering in the vapor pressure of ammonia produced by water is much less than that produced by ammonium thiocyanate of equal molecular concentration.

With regard to the vapor pressures of saturated solutions, the ratio between them and the vapor pressure of ammonia at the same temperature increases slightly with temperature, reaching a practically constant value above 10°. This is shown in the following table.

Temp T °.	P vapor pressure of saturated solution Mm.	P NH ₃ vapor pressure Mm	(P/P) × 100.
-78	1	44	2.3
-65	4	112	3.6
-50	9	323	2.8
-34	21	735	2.85
-23	34	1210	2.81
-20	41	1393	2.94
0	107	3255	3.29
10	167	4656	3.59
20	237	6480	3.66
30	316	8808	3.59
40	411	11722	3.51

At higher temperatures, it is probable that the ratio would again decrease, due to the increasing solubility of the salt.

Application of the Results.

As a means of condensing ammonia, ammonium thiocyanate could hardly displace water except when it is desirable to avoid the presence of water vapor. This is the case in the production of ammonia from nitrogen and hydrogen. From the data which have been given, it is possible to calculate at least approximately the efficiency of thiocyanate for this purpose, provided the pressure and composition of the equilibrium mixture of nitrogen, hydrogen and ammonia are known.

Assuming a mixture of the 3 gases containing 3 volume per cent. of ammonia at a total pressure of 100 atmospheres, which appears to be the minimum pressure used industrially, the percentage of ammonia which could be extracted at different temperatures is given in the table below. This table assumes that ammonium thiocyanate is in excess, so that the resulting liquid has the minimum vapor pressure.

Temp T°	NH ₃ Liquefiable %
0	95.4
10	92.7
20	89.6
30	86.1
40	82.0

The presence of nitrogen and hydrogen under high pressure might affect these values somewhat, but there are no data to show what the effect would be. A higher total pressure or a greater percentage of ammonia in the equilibrium mixture would of course increase the yields.

The liquid giving these high yields is saturated with ammonium thiocyanate and contains a relatively small percentage of ammonia. The liquid could be enriched in ammonia by some multiple system. As an illustration, at 10° , $\frac{2}{3}$ of the ammonia could be removed, giving a liquid containing 39% of ammonia instead of 22.5%. The remaining ammonia could then be removed, up to a maximum of 92.7%, by passing the gases through excess of thiocyanate.

Removal of ammonia from the liquid, when once the latter has been formed, offers no difficulty. It can be done by reducing the pressure or raising the temperature, or both. Provided the temperature is not raised sufficiently to melt the thiocyanate (150°), causing a partial transformation into thiourea, there seems no reason why the salt could not be used over again indefinitely.

Compared with the maximum amounts of ammonia which can be obtained from the equilibrium mixtures by simple refrigeration without the presence of thiocyanate, the results which have been given are striking. Assuming the same composition and pressure of the equilibrium mixture as above, and Regnault's values for the vapor pressure of liquid ammonia, the ammonia which can be recovered by refrigeration alone is

Temp. T° .	NH ₃ recoverable by refrigeration. %
0 and above	none
-10	6.0
-15	25.3
-20	39.0
-25	51.7
-30	62.0

If, however, refrigeration be adopted in the presence of ammonium thiocyanate, the results would be as follows:

Temp. T° .	NH ₃ recoverable. %
-20	98.1
-30	98.9
-50	99.6

In the practical application of this method for the absorption of ammonia, it will be found that the heat evolved by the absorption will use up a considerable quantity of the refrigerating substance. This can, however, be eliminated by carrying on the operation of absorption in several stages.

If the first absorption cylinder containing ammonium thiocyanate be maintained at 20° , the heat produced by the absorption can be easily removed by cooling with water. The ammonia recovered will represent 89.6% of the ammonia in the gas. If the second cylinder be maintained at 0° , a further quantity of ammonia equal to 5.8% will be removed. If a third cylinder be maintained at -20° , an additional quantity of ammonia represented by 2.7% of the total amount will be obtained. In the two latter stages, a system of heat interchangers may be used to maintain the efficiency of the refrigerating materials.

By such a system of absorbers it will be possible to remove 98.1% of the ammonia in the gas. Further, the heat produced by absorption of 89.6% of the ammonia will not require to be taken care of by refrigerating material.

Further work on this system combined with ammonium nitrate and with water is in progress.

Summary.

1. The vapor pressures of solutions of ammonium thiocyanate in ammonia have been determined at various temperatures between 0° and 40° .
2. The vapor pressures of a solution of ammonia saturated with ammonium thiocyanate have been determined between $+20^{\circ}$ and -78° .
3. The solubility of ammonium thiocyanate in ammonia has been found at temperatures ranging from 0° to 50° .
4. The specific conductance of several solutions at 0° has been measured.

quires. Probable causes of this abnormal lowering have been considered.

6. The practical application of the use of ammonium thiocyanate in the absorption of ammonia has been considered.

NEW HAVEN, CONN., and TROY N. Y.

THE COPPER FLAME TEST FOR HALOGENS IN AIR.¹

BY ARTHUR B. LAMB, P. W. CARLETON, W. S. HUGHES AND L. W. NICHOLS.

Received October 30, 1919

The Beilstein² test for halogens depending on the green color which copper imparts to a colorless flame in which they are present has been widely used as a sensitive test for halogens and halogen compounds in air and in other gases. A usual procedure in such cases has been to feed the gas in question into a Bunsen flame in which a spiral copper wire or a copper gauze is suspended. It has been found that by a careful regulation of the flame as little as one part in a hundred thousand parts of air can be detected in this way.

Of late this method has been widely used, at least in the laboratory, for detecting toxic war gases in air, since they almost invariably contain halogens. The delicacy mentioned above is adequate for most war gases, but for certain of the more toxic ones, for example, mustard gas, 10- to 100-fold greater delicacy is desirable. The attempt was therefore made to increase the delicacy of the copper flame test sufficiently to meet these requirements.

This has been accomplished by the very simple expedient of making the test a *cumulative* one. The air in question is passed over a moderately heated copper spiral or gauze for some time—a longer time the lower the concentration of the halogen. After this period of accumulation the copper spiral is sharply heated in a suitable flame and the green tinge observed.

Apparatus and Procedure.

The apparatus used in this test is very simple; it consists merely of a quartz tube of about one cm. bore, in which is placed a roll of oxidized copper gauze 50 meshes to the linear inch, 10 to 11 cm. long, wound tightly around a stiff iron wire, which serves as a handle for the insertion and withdrawal of the roll from the tube. In addition a non-luminous Bunsen or acetylene flame is required.

To carry out a test the air in question is drawn through the tube, while

¹ Published with the approval of Major General W. L. Sibert, Director, Chemical Warfare Service, U. S. A.

² *Beilstein Rep.* 2, 620 (1872); Noelting (interference of pyridine), *Ibid.*, 23, 3664.

the end of the copper roll near the inlet is heated from without to incipient redness. After a suitable period of accumulation the roll is removed from the tube and inserted into a colorless flame. To obtain the best results the copper roll should be introduced not too slowly into the flame, heated end first, the observer watching against a dark background whether any coloration is produced anywhere along the roll. If a non-luminous acetylene flame is used, care must be taken not to melt the copper gauze even superficially, for this results in the production of a green color in the absence of a halogen. After a positive test, by careful heating, all of the green color will usually disappear and the roll is then ready for another test.

Delicacy of the Test. Influence of Different Factors.

To determine the sensitiveness of this test and the influence of different factors such as rate of flow, concentration and temperature upon it, air-halogen mixtures of known concentrations were prepared and the time of accumulation required to give a positive test under different conditions was measured. To obtain with precision the minute concentrations of halogens required, air was passed at a known rate through a saturator containing β -dichloro-diethylsulfide ("mustard gas"), and then mixed in a mixing chamber with a stream of pure air flowing at a known and much more rapid rate. The temperature of the saturator was controlled, and since the vapor pressure of this highly involatile liquid is well known,¹ this gave a known concentration of halogen before dilution in the second air stream. As the rates of flow of the two streams were controlled by delicate valves and were measured by two sensitive flowmeters, the concentration in the dilute gas stream was also accurately known. This arrangement usually provided a more abundant stream of halogen-laden air than was required or was desirable for the test; a mixing chamber was, therefore, provided with an exit opening freely to the hood, and the required amount of mixture as indicated by a third flowmeter was drawn off from the mixing chamber into the quartz testing tube. By this simple means concentrations of chlorine between 0.0003 and 0.003 mg./l., probably accurate to 2 or 3%, were readily secured. A diagram of the whole apparatus is given in Fig. 1.

¹ Vapor Pressure of β -Dichloro-diethylsulfide, and Concentration of its Saturated Vapor.

Temp. ° C.	Vapor pressure. mm. Hg	Concentration of vapor			
		Dichloro-diethylsulfide		Chlorine	
		P P M	Mg./L.	P P M.	Mg./L.
0	0.025	33	0.22	33	0.10
10	0.040	53	0.36	53	0.16
15	0.047	62	0.42	62	0.19
20	0.062	82	0.54	82	0.24
22	0.064	84	0.56	84	0.26

TABLE I.
Delicacy of Test for Chlorine.

Rate of flow L./min.	Time of ac- cumulation Min.	Temp °C	Total chlorine Mmg.	No of trials.	Minimum chlo- rine detected. Test. Mmg.	Remarks.
Approximate Concentration, 0.5 P. P. M., or 1.45 mmg./L.						
1.5	2	25	9.3	4	+	4.0 Faint
1.5	1	25	4.7	7	+	
1.5	1	25	4.7	4	=	
Approximate Concentration, 0.2 P. P. M., or 0.58 mmg./L.						
1.5	4	25	3.5	3	+	2.6 Faint
1.5	3	25	2.7	2	=	
4.0	3	25	7.1	2	+	7.1
4.0	3	25	7.1	2	-	
8.0	3	25	14.2	4	+	9.3 Faint
8.0	2	25	9.5	2	=	
Approximate Concentration, 0.1 P. P. M., or 0.29 mmg./L.						
1.5	6	23	2.4	2	+	2.4
1.5	6	27	2.8	1	+	
1.5	5	27	2.3	1	-	
4.0	3	27	3.7	2	+	< 3.7
8.0	5	28	12.8	1	+	
8.0	5	26	12.0	3	+	
8.0	3	27	7.4	1	+	5.5
8.0	3	26	7.2	1	+	
8.0	3	22	6.0	3	+	
8.0	2	27	5.0	2	-	
Approximate Concentration, 0.05 P. P. M., or 0.145 mmg./L.						
1.5	20	25	4.4	1	+	2.3
1.5	15	25	3.3	1	+	
1.5	11	25	2.4	2	+	
1.5	10	25	2.2	2	-	
4.0	11	26	6.6	2	+	2.8
4.0	10	26	6.0	1	+	
4.0	7	26	4.2	2	+	
4.0	5	28	3.2	1	+	
4.0	5	26	3.0	2	+	Faint
4.0	5	24	2.8	1	=	Faint
4.0	4	24	2.2	2	-	Faint
8.0	11	26	13.2	1	+	5.0
8.0	10	26	12.0	4	+	
8.0	5	24	5.6	4	+	
8.0	4	24	4.5	2	-	
Approximate Concentration, 0.01 P. P. M., or 0.029 mmg./L.						
4.0	36	27	4.5	1	+	2.8
4.0	23	27	3.1	1	+	
4.0	20	27	2.4	1	-	

The results obtained are collected in Table I. In this table the concentrations are given both in parts per million by volume (P. P. M.) and in thousandths of a milligram (mmg./l.) per liter, at rates of flow between 1.5 and 8 liters per minute. The temperatures of the dichloro-diethyl-sulfide are recorded and from these data and the known length of the

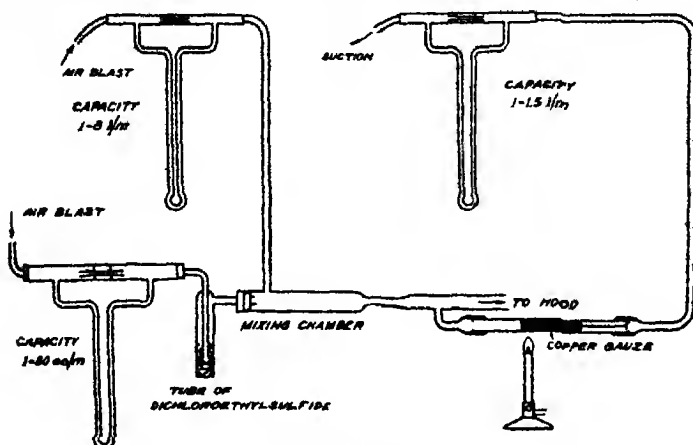
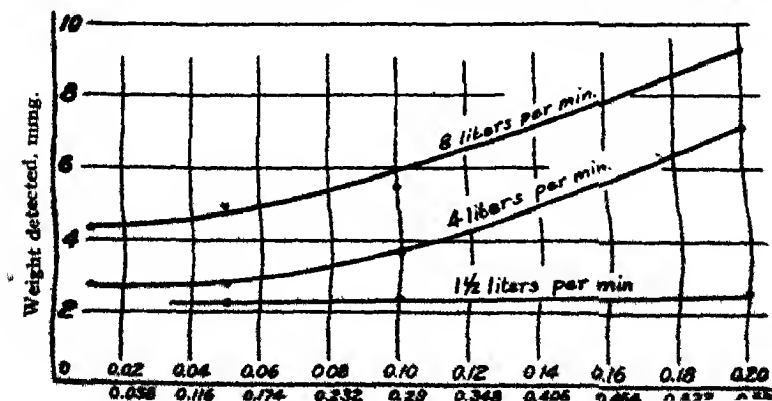


Fig. 1.—Apparatus.

period of accumulation the total chlorine passing over the copper gauze during this period was computed and is given in Col. 4. The positive or negative test obtained is indicated in Col. 6, respectively by plus and minus signs. From these results the minimum amounts of chlorine detected, expressed in thousandths of a milligram, are derived and given in Col. 7.

In Fig. 2 these minimum amounts detected are plotted against concentrations at 3 different rates of flow. This figure indicates that, as would



be expected, the slower the rate of flow the smaller the absolute amount of chlorine which can be detected. At the slowest rate tried, namely, 1.5 liters per minute, the least amount which could be detected would be 0.0022 mg., and as there is little gain in passing from 4 to 1.5 liters per minute, it is improbable that even by a very much slower rate of flow anything less than 0.002 mg. of chlorine could be detected. This would seem to imply that it requires at least this amount of chlorine to produce a noticeable green color under the above conditions. Fig. 2 further shows that the delicacy at low rates of flow is substantially independent of the concentration, but that at high rates of flow the delicacy is greatest at low concentrations. A simple explanation of this fact would be that beyond a certain critical velocity more or less of the halogen escapes absorption by the copper during the period of accumulation.

Experiments were next made to determine how close a regulation of the temperature of the copper spiral during the period of accumulation was necessary. In the regular procedure followed in securing the above results, the quartz tube was heated to redness on the lower side for 12 to 25 mm., directly underneath the tip of the copper gauze cylinder. A series of duplicate experiments were now run in which the quartz tube was heated much more strongly, namely, to redness for a distance of 38 mm. underneath the end of the copper spiral. Care was taken, nevertheless, to avoid a temperature high enough to volatilize the copper chloride along the entire length of the copper gauze cylinder. No difference could be observed in the sensitiveness of the test under the two conditions.

Duplicate measurements were also made comparing the above copper gauze of 50 meshes to the inch, with a much finer gauze, namely, one of 150 meshes to the inch. A very slight decrease in sensitiveness was observed, presumably due to the increased resistance to the free passage of air through the gauze and hence to the greater tendency for rapid passage of the gas through the larger channels between the copper spiral and the quartz tube. A further objection to the use of the finer mesh was the increased ease with which it melted when slightly superheated, which not only vitiated the results, but produced a deformation of the gauze cylinder, and a consequent increase in leakage.

The "age" of the copper gauzes was, on the other hand, found to be of some importance. A new, bright gauze was found to be less sensitive than one which had been in use for some time. After a number of tests had been made on a gauze no distinction could be observed. This behavior is doubtless due to the formation of a more active surface as the result of the alternate oxidations and reductions incident to the test; indeed it is very likely connected with the known highly absorbent nature

Approximate Estimation of Concentration.

The results obtained proved to be so reproducible that it seemed worth while to determine whether this method could be employed to estimate roughly very low concentrations of chlorine and chlorine compounds in air. Evidently, the most convenient way to do this would be first to plot curves, based on the previous results, showing at different rates of flow the periods of accumulation required to give a positive test at different concentrations. This has been done in Fig. 3. Then, in case of an unknown concentration, one need only determine the minimum

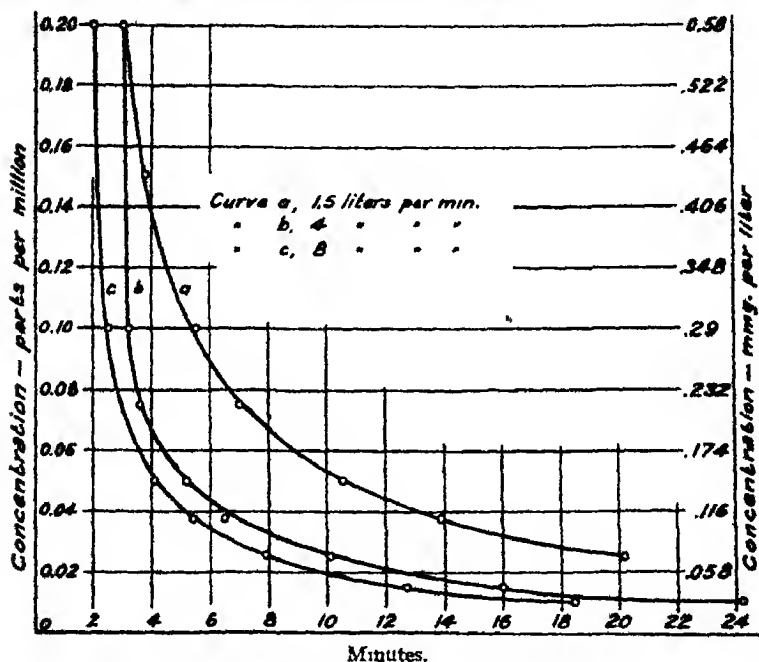


Fig. 3.—Relation between concentration and time of accumulation.

period of accumulation required for a positive test at a given rate of flow and read off from the appropriate curve the concentration which must have prevailed during the period of accumulation. Fig. 3 shows that in general it will be more advantageous to determine relatively high concentrations (0.003 mg./l. and higher) at low rates of flow (1.5 liter per minute); while lower concentrations, because of the long periods of accumulation required, are more conveniently determined at relatively high rates of flow.

To determine the usefulness of this method of approximate analysis, the series of tests given in Table II were carried out at moderate concentrations of hal-

twenty and one part in ten million parts of air. By comparison of Cols. 10 and 11 of the table it will be seen that there is a close concordance between the concentrations of the gas mixtures actually used and those predicted by the curve from the times of accumulation required for a positive test.

TABLE II.
Approximate Estimation of Chlorine Compounds in Air.

Rate of flow L./min	Temp °C.	Concentration		Time of accum Min	Total chlorine. Mmg	No of tests	Result of tests	Minimum time for positive test Min	Concentration.	
		P. P. M	Mmg /L						Actual. Mmg /L	From curve. Mmg./L
Approximate Concentration, 0.05 P. P. M										
1.5	25	0.050	0.147	11	2.4	3	+	10.5	0.15	0.14
1.5	25	0.050	0.147	10	2.2	2	—			
4.0	25	0.050	0.147	7	4.1	2	+	5.2	0.15	0.14
4.0	25	0.050	0.147	5	3.0	5	±			
8.0	25	0.050	0.147	5	5.9	4	+	4.6	0.15	0.14
8.0	26	0.052	0.152	4	4.9	2	—			
Approximate Concentration, 0.1 P. P. M										
1.5	24	0.095	0.28	7	2.9	4	+	6.0	0.28	0.27
1.5	24	0.095	0.28	7	2.9	1	—			
1.5	24	0.095	0.28	6	2.5	7	+			
1.5	24	0.095	0.28	6	2.5	2	—			
8.0	24	0.10	0.28	3	7.0	5	+	2.5	0.31	0.29
8.0	28	0.112	0.32	2	5.1	2	—			

As this method depends on the estimation and detection of faint color, it will always require experience and a preliminary calibration, so to speak, of the operator. It would, of course, be possible to arrange for a simultaneous comparison of the air in question with an air mixture containing a known concentration of halogen, but the essentially qualitative nature of the method seemed hardly to justify the additional complexity and difficulty.

Summary.

By the simple expedient of making it cumulative the copper flame test for halogens in air has been rendered much more sensitive, so that a little as one part of halogen in fifty or a hundred million parts of air is readily detected. Moreover, the simplicity and rapidity of the test have not been sacrificed in the process.

The results are sufficiently definite and reproducible to permit a fairly close estimate of the concentration of the halogen from the length of the accumulation period required to give a positive test.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THROOP COLLEGE OF TECHNOLOGY No. 6.]

THE CRYSTAL STRUCTURES OF WULFENITE AND SCHEELITE.

By ROSCOE G. DICKINSON

Received November 10, 1919

1. Introduction.

Wulfenite, PbMoO_4 , and scheelite, CaWO_4 , are substances showing both chemical and crystallographic similarities. Both crystallize in the tetragonal system, and the two crystals possess nearly equal axial ratios. Wulfenite is placed by Groth¹ and by Tutton² in the pyramidal or hemimorphic-hemihedral class, the class of lowest possible tetragonal symmetry, characterized by the possession of a tetragonal axis only. Scheelite is placed by Groth and by Tutton in the bipyramidal or pyramidal-hemihedral class, which, in addition to a tetragonal axis, possesses a symmetry plane perpendicular to that axis. According to Dana's "Mineralogy"³ the etch figures of wulfenite do not, however, show hemimorphism, i. e., lack of the equatorial symmetry plane.

At all events wulfenite and scheelite possess considerably less symmetry than other tetragonal crystals of similar composition, such as rutile, anatase, cassiterite, zircon, and xenotime, which have been studied by Vegard⁴ and by Williams.⁵ Thus a knowledge of the structure of these substances would, in addition to giving information on the general problem of interatomic forces, show what dissymmetry in the atomic arrangement, if any, corresponds to the dissymmetry of the crystalline substances. Whereas this research has not led to a complete solution of the structure, enough information has been obtained to make a discussion profitable, and to indicate some of the difficulties of the application of the Bragg method, in its present stage of development, to other than fairly simple crystals.

2. Apparatus and Procedure.

The apparatus is essentially the same as that used by Burdick and Ellis⁶ in the study of chalcopyrite in this laboratory. One modification used in the later part of the investigation deserves mention. Instead of reading the electroscope directly by means of a microscope provided with an optical micrometer, as was done in some of the measurements on wulfenite, the position of the shadow of the electroscope-leaf projected on a screen was read. This was accomplished by placing behind the

¹ *Chemische Kristallographie*.

² *Crystallography and Practical Crystal Measurement*. MacMillan, 1911.

³ *Mineralogy*, 1900, Appendix I, p. 74.

⁴ *Phil. Mag.*, 33, 395 (1917); 33, 65 (1916); 32, 505 (1916).

⁵ *Proc. Roy. Soc. (London)* 123, 112 (1928).

electroscope an electric lamp and collimator; in front of the electroscope was placed the microscope in the usual manner, but with the eyepiece

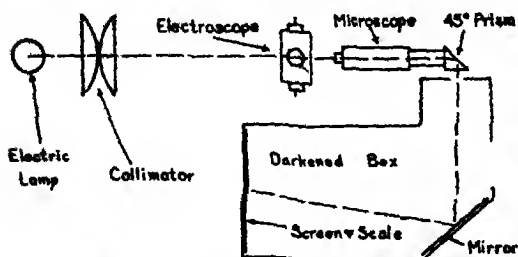


Fig. 1.—Plan of apparatus for projecting image of electroscope leaf.

both eyes at the distance of normal vision. This eliminated the eye-strain to a considerable extent.

The wulfenite crystal used was loaned by Prof. W. H. Clapp, of this College. It was of tabular habit with 001 and 102 faces considerably developed. It was 16 mm. wide by 4 mm. thick. The color was bright orange-red.

Two of the scheelite crystals (marked A and B in the table of results) were loaned by the Smithsonian Institution and came from Korea. Both had only the 101 faces developed. A weighed over 50 g. A was grey in color, while B was brown.

Only 3 of the spectra measured (*viz.*, 001 and 102 from wulfenite and 101 from scheelite) were obtained from developed faces. In other cases it was attempted to set the crystal in such a way that reflection would take place without making it necessary for the X-ray beam to pass through any considerable amount of crystal; for, owing to the high absorption coefficients of lead and tungsten, the relative intensities of the successive orders might be considerably affected if the amount of crystal the beam passed through were different for different orders.¹ For instance, the 100 spectrum with scheelite was obtained by setting the crystal with its tetragonal axis vertical, reflection taking place in the region of the horizontal intersection of two 101 faces. In some cases the crystal was ground to have the desired face.

The usual procedure was to find the proper setting of the crystal for a maximum by moving the crystal while keeping the chamber open wide; then to determine the chamber angle with the chamber slit narrowed, usually to one mm. When the crystal and chamber angles for one maximum were thus determined, the entire region between 0 and 60° (chamber angle) or more was examined for other maxima by moving the chamber with its slit at 2 mm. through successive small angles and moving

¹ See W. H. Bragg, *Phil. Mag.*, 27, 833 (1914).

the crystal half as fast. After the existence of various maxima was shown the precise position of each was more carefully determined. Finally, with the chamber-slit at 2 mm., the intensities of the maxima were measured in rapid succession. The width of the slit next to the crystal was kept usually at 2 mm., but for some weak spectra it was opened to 4 mm.

3. Treatment of the Observations.

Owing to the fact that the effective reflecting plane is not always at the center of the graduated circle (especially when the face in question is not developed on the crystal), the zero position of the ionization chamber is not at 0° but at some small angle φ_0 . For any two orders of reflection, say the a th and the m th, the value of φ_0 , which must be chosen in order to bring the observed chamber angles φ_a and φ_m into accord with the equation $n\lambda = 2d \sin \varphi_n/2$ is given by the equation

$$\tan \varphi_0/2 = \frac{m \sin \varphi_a/2 - a \sin \varphi_m/2}{m \cos \varphi_a/2 - a \cos \varphi_m/2}.$$

As a result of experimental error and of the fact that the effective reflecting plane of an imperfect crystal does not remain constant as the crystal is rotated, the values of φ_0 calculated from different pairs of maxima are not always equal, and they sometimes show progressive variation. Consequently, instead of calculating φ_0 from an arbitrarily

TABLE I.—REFLECTION DATA FOR WULFENITE

Plane	Order n	Half of observed chamber angle	Zero point $1/2 \varphi_0$	Corrected angle of reflection, $1/2 \varphi_n$	$\sin 1/2 \varphi_n$	$1/n \sin 1/2 \varphi_n$	Relative intensity
101	I	$5^\circ 3'$	$-12'$	$5^\circ 15'$	0.0915	0.0915	100
	II	$10^\circ 20'$		$10^\circ 32'$	0.1828	0.0914	66
	III	$15^\circ 47'$		$15^\circ 59'$	0.2754	0.0918	30
	IV	$21^\circ 15'$		$21^\circ 27'$	0.3657	0.0914	13
	V	$26^\circ 53'$		$27^\circ 5'$	0.4553	0.0911	5
100	I	$8^\circ 45'$	$0'$	$8^\circ 45'$	0.1521	0.1521	100
	II	$17^\circ 49'$		$17^\circ 49'$	0.3060	0.1530	26
	III	$27^\circ 0'$		$27^\circ 0'$	0.4540	0.1513	4
110	I	$6^\circ 5'$	$-5'$	$6^\circ 10'$	0.1074	0.1074	91
	II	$12^\circ 22'$		$12^\circ 27'$	0.2156	0.1078	100
	III	$18^\circ 45'$		$18^\circ 50'$	0.3228	0.1076	50
001	I	$5^\circ 27'$	$-8'$	$5^\circ 35'$	0.0973	0.0973	100
	II	$11^\circ 7'$		$11^\circ 15'$	0.1951	0.0976	60
	III	$16^\circ 48'$		$16^\circ 56'$	0.2913	0.0971	46
	IV	$22^\circ 45'$		$23^\circ 53'$	0.3889	0.0972	11
111	III	$9^\circ 58'$	$-28'$	$10^\circ 26'$	0.1811	0.0604	16
	IV	$13^\circ 30'$		$13^\circ 58'$	0.2414	0.0604	100
102	I*	$14^\circ 0'$	$-20'$	$14^\circ 20'$	0.2476	0.2476	100
	II	$29^\circ 30'$		$29^\circ 40'$	0.4950	0.2475	7

* A doubtful reflection of intensity 5 was obtained when half the observed chamber angle was $6^\circ 45'$.

chosen pair of reflections, say the first and second orders, a value of φ_0 has been sought for the series of spectra from each plane so as to give the least possible variation to the quantity $1/n \sin \varphi_n/2$ where φ_n is the corrected chamber angle.

The small amount of stray reflection in the neighborhood of the maxima has been subtracted in determining the relative intensities.

4. The Observed Values.

The experimental results are given in Tables I and II, of which the headings are self-explanatory.

TABLE II.—REFLECTION DATA FOR SCHRELITE.

Plane	Order, n	Half of observed chamber angle	Zero point, $\varphi_0/2$	Corrected angle of reflection, $1/2 \varphi_n$	$\sin 1/2 \varphi_n$	$1/n \sin 1/2 \varphi_n$	Relative intensity.
101	I	$5^\circ 20'$	$-7'$	$5^\circ 27'$	0.0950	0.0950	100
A	II	$10^\circ 52'$		$10^\circ 59'$	0.1905	0.0953	59
	III	$16^\circ 30'$		$16^\circ 37'$	0.2860	0.0953	18
	IV	$22^\circ 15'$		$22^\circ 22'$	0.3805	0.0951	8
100	I	$8^\circ 45'$	$-30'$	$9^\circ 15'$	0.1607	0.1607	100
A	II	$18^\circ 22'$		$18^\circ 52'$	0.3234	0.1617	28
	III	$28^\circ 23'$		$28^\circ 53'$	0.4830	0.1610	8
110	I	$6^\circ 40'$	$-15'$	$6^\circ 25'$	0.1118	0.1118	67
B	II	$13^\circ 14'$		$12^\circ 59'$	0.2247	0.1123	100
	III	$19^\circ 52'$		$19^\circ 37'$	0.3357	0.1119	49
	IV	$26^\circ 48'$		$26^\circ 33'$	0.4457	0.1114	25
	V	$34^\circ 17'$		$34^\circ 2'$	0.5597	0.1119	8
001	I	$6^\circ 8'$	$-10'$	$5^\circ 58'$	0.1040	0.1040	75
A	II	$12^\circ 11'$		$12^\circ 1'$	0.2082	0.1041	100
	III	$18^\circ 22'$		$18^\circ 12'$	0.3124	0.1041	82
	IV	$24^\circ 38'$		$24^\circ 28'$	0.4142	0.1037	19
111	I	$3^\circ 19'$	$-10'$	$3^\circ 29'$	0.0608	0.0608	weak
A	III	$10^\circ 33'$		$10^\circ 43'$	0.1860	0.0620	26
	IV	$14^\circ 12'$		$14^\circ 22'$	0.2481	0.0620	100
	V	$17^\circ 49'$		$17^\circ 59'$	0.3087	0.0617	4
VIII		$29^\circ 22'$		$29^\circ 32'$	0.4929	0.0616	11

5. Interpretation of the Crystal Structure.

The various planes of atoms parallel to a possible crystal face constitute an array that may be formed by the indefinite repetition of a pattern made by a small number of planes. The thickness of the thinnest possible pattern of this character will be called here the interplanar distance. An example is shown in Fig. 3. It will be noticed that interplanar distance as here defined is not the distance between two adjacent planes, nor even the smallest distance between two similarly constituted planes. Since the entire atomic array may be considered to be made up of atoms on several equal interpenetrating lattices, the distance calculated from the formula $n\lambda = 2d \sin \varphi_n/2$ cannot be larger than that between two ad-

jacent planes of one lattice;¹ it is equal to it, or is a small submultiple of it. On the other hand, the crystallographic ratios must be obtainable from the ratios of the corresponding *lattice* distances by multiplication by small integers; hence the crystallographic ratios are obtainable also from the interplanar distances, as above defined, by multiplication by small integers.

If $c : a$ is the crystallographic ratio of a tetragonal crystal, then $nc : ma = d_{001} : d_{100}$, where n and m are small integers. From the fundamental equation for reflection it follows that $d_{001} \cdot d_{100} = \sin (\varphi/2)_{100} : \sin (\varphi/2)_{001}$. For wulfenite this becomes $0.1521/0.0973 = 1.563$. From crystallographic data $c : a = 1.577$. For scheelite we have $0.1611/0.1040 = 1.549$, while crystallographic data give 1.536. Evidently in each case n and m may be taken as unity.

We may now investigate the type of lattice underlying the atomic arrangement. It will be convenient to find various simple arrangements that make the ratio of d_{001} to d_{100} equal to the crystallographic ratio and to choose from these the arrangement that gives the observed ratios of the other interplanar distances.

There are only two distinct lattices having tetragonal symmetry. One is formed by placing points at the vertices of a rectangular parallelepiped with a square base; the other is formed by placing points at the vertices and at the center of the faces of a rectangular parallelepiped with a square base. Various relative interplanar distances, however, may be obtained by arranging these lattices differently with respect to the crystallographic axes, or by allowing two or more identical lattices to interpenetrate at rational fractions of some lattice interplanar distance. Six cases will be considered.

Case I. The lattice is formed by placing points at the vertices of rectangular parallelepipeds with square bases, the crystallographic axes coinciding in direction with the edges of the parallelepipeds.

Case II. The same as Case I, except that the two equal crystallographic axes are at 45° with the edges of the square base of the parallelepiped.

Case III. The lattice is formed by placing points at the vertices and centers of the faces of rectangular parallelepipeds with square bases, the crystallographic axes coinciding in direction with the edges of the parallelepiped.

¹ It will be observed that the term "lattice" or "space-lattice" is here used in the strict sense given it by crystallographers and also given by W. H. and W. L. Bragg in their book, "X-Rays and Crystal Structure." The following definition is from Harold Hilton, "Mathematical Crystallography." "A series of parallel planes such that the distance between any two consecutive planes is constant and equal to a will be called a set of planes of interval a . The sum total of the points of intersection of any three sets of planes is called a 'regular space-lattice,' or more simply a 'lattice.'" It seems desirable to avoid the loose terminology of many X-ray investigators.

Case IV. The same as Case III, except that the two equal crystallographic axes are at 45° with the edges of the square base of the parallelepiped.

Case V. Two lattices each arranged as in Case III interpenetrating in such a way that a point of the second lattice is situated on a diagonal of the first, one-quarter of the distance between two points of the first.

Case VI. The same as Case V, except that the two equal crystallographic axes are at 45° with the edges of the square base of the parallelepiped.

The ratios of the various interplanar distances may now be calculated starting in each case with $d_{001} \cdot d_{100} = c \cdot a$ or simply c . For the planes studied there is some distinction between any two of the above cases. It is found that agreement with the observed ratios is obtained in Case V and in no other. For Case V the ratios $d_{001} : d_{100} : d_{110} : d_{101} : d_{111} : d_{102}$ may be calculated with aid of the expressions

$$c : 1 : \sqrt{2} : \frac{2}{\sqrt{1 + 1/c^2}} : \frac{4}{\sqrt{2 + 1/c^2}} : \frac{1}{\sqrt{1 + 4/c^2}}$$

The ratios so calculated from crystallographic data are to be compared with the ratios of the reciprocals of the sines of the glancing angles.

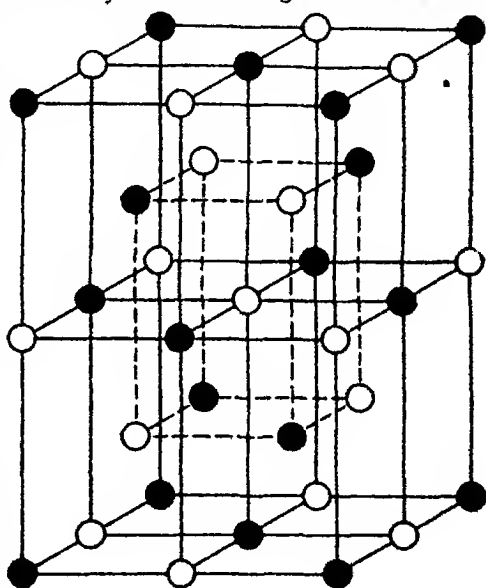
In the case of wulfenite we have for $d_{001} : d_{100} : d_{110} : d_{101} : d_{111} : d_{102}$, from crystallographic data: 1.577 : 1.1414 : 1.689 : 2.581 : 0.619; from X-ray reflection data: 1.563 : 1.1414 : 1.666 : 2.522 : 0.615.

In the case of scheelite we have for $d_{001} : d_{100} : d_{110} : d_{101} : d_{111}$, from crystallographic data: 1.536 : 1.1414 : 1.676 : 2.569, from X-ray reflection data: 1.549 : 1.1440 : 1.692 : 2.598.

Before proceeding further we will investigate whether this arrangement is in agreement with the observed densities of the crystals. To do this it is necessary to note the number of atoms associated with some arbitrary unit volume of the structure. Consider for each of the 6 cases a parallelepiped whose dimensions are the interplanar distances d_{100} , d_{100} , d_{001} . The number of PbMoO_4 or of CaWO_4 groups associated with it is in: Case I, one, Case II, one half, Case III, one-half; Case IV, one-quarter; Case V, one-eighth; Case VI, one-quarter. The value of d_{001} which must be taken in order to give this number x atom groups in a volume equal to $(d_{100})^2 \times (d_{001})$ cc is given by the expression: $d_{001} = \sqrt[3]{xMc^2/\rho N}$, where M is the formula weight, c is the crystallographic ratio, ρ is the density, and N is Avogadro's number. For wulfenite ρ was found to be 6.82, and for scheelite 6.06. This gives, placing x equal to one-eighth, d_{001} for wulfenite equal to 3.02×10^{-8} cm., and for scheelite equal to 2.85×10^{-8} cm. Values of d_{100} may also be obtained from the X-ray data by placing, for the palladium target, $\lambda = 0.584 \times 10^{-8}$ cm., in the expression $n\lambda = 2d \sin \frac{1}{2}\theta$. This gives for wulfenite 3.00×10^{-8} , and for scheelite 2.81×10^{-8} cm.

It is thus evident that Case V gives not only the correct ratios of the distances between various planes, but also the proper absolute values of those distances to accord with the density of the crystals. So far, then, it has been demonstrated that the lattice upon which the crystal is built is the face-centered, and that the metal atoms (*e. g.*, the lead atoms) are associated in pairs with each point of the lattice in such a way as to produce the arrangement described under Case V. This arrangement has often incorrectly been termed a "diamond lattice."

The next step will be to locate the molybdenum atoms with respect to the lead atoms, and the tungsten atoms with respect to the calcium atoms. It may be seen that the only kind of tetragonal rotation axis possessed by the diamond arrangement is a tetragonal screw axis. If it is desired to superpose two such arrangements (*e. g.*, the lead atoms and molybdenum atoms) in such a way that the resulting arrangement will have a tetragonal axis, it is evidently necessary to bring into coincidence the tetragonal screw axes of each of the separate arrangements. Similarly the only equatorial symmetry plane possessed by a tetragonal diamond arrangement is a glide reflection plane. If these also are brought into coincidence (scheelite it will be remembered, possesses an equatorial plane), the arrangement shown in Fig. 2 is obtained.



● Pb or Ca Atoms; ○ Mo or W Atoms.

Fig. 2.—Arrangement of metal atoms in wulfenite and scheelite.

By far the most striking abnormality in the relative intensities of successive orders of reflection was found in the case of the 111 plane. With each crystal the fourth order was found to be by far the strongest of all. In the case of scheelite, which gave somewhat stronger 111 reflections than wulfenite, it was also found easily possible to locate the eighth order, whereas the sixth and seventh could not be found. It will now be shown that the chosen arrangement of molybdenum atoms relative to lead atoms and of tungsten atoms relative to calcium atoms accounts for this great

abnormality. The oxygen atoms, certainly in the case of wulfenite, are too small compared with the other atoms to account for it.

The arrangement of the planes of atoms that are parallel to the 111 face is, leaving the oxygens out of consideration, shown in Fig. 3. The distance corresponding to first-order reflection is also indicated on the figure.



Fig. 3 — Diagrammatic representation of spacing of 111 planes

It can readily be seen that for first-order reflection there is considerable interference; in the second order this interference amounts to annihilation; in the third order there is interference to the same extent as in the first; but that in the fourth order all of the planes reinforce each other.

The cycle is then repeated, complete reinforcement occurring again in the eighth order. This is a very sensitive test of the arrangement.

As far as we have proceeded, the structure will be seen to be of the same type as the structure assigned to zircon and to xenotime by Vegard. The remaining problem is the location of the oxygen atoms, and here no very satisfactory solution can be claimed. The arrangement of the oxygen atoms in wulfenite or scheelite cannot be the same as the arrangement in either zircon or xenotime, for the observed 001 spectra are not normal as this would require. Nor can it be the same as assigned by Vegard to anatase, for this would require for 110 a normal spectrum.

An examination of the arrangement of the heavy atoms (*e. g.*, those of lead and molybdenum) shows that this arrangement possesses holohedral symmetry. Thus it has a tetragonal screw axis with 4 symmetry planes parallel to it, two of which are reflection planes and two are glide reflection planes, also an equatorial glide reflection plane with 4 diagonal axes parallel to it. It thus becomes evident that the dissymmetry of the crystalline substances is to be accounted for, either by the assumption of dissymmetry of the atoms themselves, or more likely by dissymmetry in the arrangement of the oxygen atoms.

Some of the difficulty of further interpretation is illustrated by the spectra from the 110 planes. The relative intensities of the first 3 orders are for wulfenite, 91 : 100 : 50, and for scheelite, 67 : 100 : 49. For the calculation of the relative intensities that a given arrangement may be expected to produce three assumptions are in accord with much of the published data: (1) Each atom contributes to the amplitude of the resultant wave an amount that is proportional to its atomic number, the resultant being found in the usual manner of vector composition. (2) The intensity is proportional to the square of the resultant amplitude. And (3), the intensity is proportional to that which would be obtained from a set of equally weighted, equally spaced planes. This normal ratio

of intensities has usually been taken as $100 : 20 : 7$ or sometimes $100 : 30 : 12$.¹ If for the moment we neglect the requirements of symmetry and place the oxygen atoms in planes half way between those already formed by the other atoms, we have an arrangement which will give as strong a second order as possible relative to the first. Taking as the normal ratios the more favorable values $100 : 30 : 12$, the calculated intensities become $100 : 86 : 12$ and $81 : 100 : 10$, respectively. Even for this best arrangement the second order is not strong enough, and the third order is far too weak. Indeed it is not possible to find any way of introducing the oxygen atoms which will make the third order strong enough on the above assumptions, and any attempt to do so necessarily weakens the second order, which at best is too small. Similar difficulties are encountered with some of the other planes.

There are several possible reasons why the above assumptions prove inadequate. It may be desirable to assume higher values for the relative intensities of the higher orders of a normal spectrum. Vegard has already done this in some cases. Possibly light atoms contribute more to the amplitude than an amount proportional to their atomic numbers. It may further well be that the reflecting power of an atom is dependent on its situation relative to neighboring atoms. On the experimental side a more precise definition of the area of crystal from which reflection takes place would be desirable.

For advice and assistance in carrying on this work the author is indebted to Dr. Arthur A. Noyes and to Dr. James H. Ellis.

6. Summary.

1. X-ray spectra from several planes of both wulfenite (PbMoO_4) and scheelite (CaWO_4) have been measured and tabulated.

2. It has been shown that the face-centered lattice with the atoms so located as to form a "diamond" arrangement accounts in each case for the relative spacings of different planes, and for the density of the crystals.

3. The arrangement of the heavier atoms relative to each other has been determined by a qualitative consideration of the relative intensities.

4. The difficulties in the location of the oxygen atoms have been discussed.

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¹ The proper set of values to choose is a matter of much uncertainty. We have found it possible to vary the ratio of the intensities of the first two orders from the 100 plane of sodium chloride from $100 : 30$ down to $100 : 15$ by narrowing the slit nearest the crystal by steps from 1 mm. to 0.1 mm.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS]

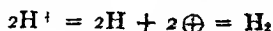
OVERPOTENTIAL AND CATALYTIC ACTIVITY.

By ERIC K. RIDEAL.

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It is well known that the catalytic activity of metals in cases of heterogeneous catalysis varies both with their natures and physical states, and in a recent communication it was pointed out that a tangible explanation for the behavior of certain metals in a case of selective oxidation was to be found in W. M. Lewis's application¹ of Krüger, Marcelin and Rice's concept of activity to Harkins and Langmuir's hypothesis of surface orientation in adsorption.

It seemed possible that another application of this concept might be found in the simplest case of heterogeneous catalysis, namely the liberation of gases at electrode surfaces. The general course of an electrode reaction may be represented by the following typical example:



making no assumption as to the possible hydration of the ions in solution. Caspari, Wilsmore, Le Blanc and others have shown that the liberation of hydrogen gas at an electrode surface is an irreversible process, or that there is always an overpotential (η volts) in excess of that demanded by the free energy relationship. Overpotentials are likewise to be found in the liberation of oxygen at anodes and in the deposition of metals and metallic hydroxides at electrode surfaces, but with the exception of the case of hydrogen where the phenomenon is well marked, little record is to be found in the literature.

Overpotential varies with the nature of the electrode, rising to high values for mercury, zinc, and lead and sinking to low values for nickel, platinum and copper.

Of the more important theories which have from time to time been advanced to explain the occurrence of overpotential, may be briefly mentioned the following:

1. The formation of unstable hydrides, a view advanced by Foerster and supported by Newbery.²
2. The variation in thickness of a poorly conducting gas film, a view originally suggested by Haber.³
3. An increased solution of hydrogen in the electrode, caused by the

¹ *J. Chem. Soc.*, 105, 2331 (1914); 107, 233 (1915); 109, 55, 67, 796 (1916); 111, 389, 457, 1086 (1917), 113, 471 (1918), 115, 182 (1919), see also Lewis and Jackson, *Proc. Am. Acad.*, 41, 397 (1906).

² *J. Chem. Soc.*, 109, 1051, 1359 (1916).

³ *Z. Elektrochem.*, 8, 539 (1902).

relative slowness with which the electrode charged with gas can get into equilibrium with the atmosphere.¹

4. The presence of monatomic hydrogen, a view supported by Bancroft² and Bennet and Thompson.³

5. The variation in the surface tension of large and small bubbles of gas with which the electrode is in equilibrium, an hypothesis advanced by Helmholtz⁴ and Möller⁵ and recently supported by MacInnes and Adler.⁶

On the adsorption theory the following view-point may be advanced. At any surface when equilibrium is established between metal and the surrounding medium, the number of molecules striking and becoming adsorbed on the surface will be equal to the number evaporating, although the actual number liberated and adsorbed per second will vary with the nature of the metal. Under these conditions the free energy equation

$$E = \frac{RT}{F} \log \frac{P}{CH}$$

will hold for all metals. On the passage of current, however, discharge of hydrogen occurs with the formation of atomic hydrogen adsorbed on the metal surface (presumably by a pair of electrons, or one valence bond). The affinity of atomic hydrogen for another atom at room temperature is so large (ca. 80,000 cal. per g. mol.) that immediate combination between neighboring atom pairs occurs, resulting in the formation of molecular hydrogen, which, however, is still attached to the metal by each atom, a hydrogen molecule occupying two elementary spaces on the metal surface. For very small currents, in rapidly agitated electrolytes and with metals which do not hold the molecules very firmly it will be evident that the rate of removal of the gas away from the surface by evaporation may quite easily approach the rate of supply of the gas ions, and no overpotential will result. On the other hand, if a molecule of hydrogen has to be vaporized before two empty spaces are left on the metal surface for the gas ions, it is evident that actual work has to be done by the gas ions in vaporizing the molecular hydrogen. Overpotential is thus primarily a measure of the energy necessary to *desorb* hydrogen gas from a metal surface. Two factors, however, permit of relatively large currents being passed for only a slight overpotential; one is the normal evaporation into an unsaturated electrolyte, similar to the so-called diffusion current, and the other is the tendency to the formation of bubbles.

¹ Nernst, *Ber.*, 30, 1547 (1897).

² *J. Phys. Chem.*, 20, 396 (1916).

³ *Ibid.*, 20, 296 (1916).

⁴ *Theorie der Wärme*, p. 309.

⁵ *Z. physik. Chem.*, 65, 226 (1909).

⁶ *This Journal*, 41, 194 (1919).

The hydrogen molecules attached to the metal surface are not at rest but are performing highly damped oscillations, and if the adsorbing forces are not too strong molecules can coalesce to form small bubbles, especially around small points, which, as has already been pointed out, will affect the electrode potential.

We should therefore expect bubble size to be an important factor in the η value when the energy of desorption per gram molecule is small, but for large values of the latent heat the molecules are less mobile and bubbles are not formed so easily, consequently bubble size should have but a small influence on the overpotential. Confirmation of this deduction was obtained from experiments, on the influence of temperature on overpotential which are detailed later.

The desorption theory of overpotential is also supported from another point of view. Calculation from Bohr's theory¹ of the structure of the hydrogen molecule indicates that 21,000 calories per gram molecule is required to remove an electron from one atom to the other in a hydrogen molecule, which, according to the theory alluded to above, is the critical energy increment of the activation of hydrogen gas in free space, being of course less than that necessary for the formation of atomic hydrogen, which requires another increment of energy. This critical energy increment can be equated to the electrical energy required to desorb a gram-molecule of gas from an electrode surface, or,

$$\frac{96,540 \times 2}{4.2} \times \eta = 21,000, \text{ or } \eta = 0.455 \text{ volt.}$$

It follows that metals having η values equal to or exceeding 0.455 volt, should, if used as catalysts in hydrogenation processes, show no activity since the energy necessary for desorption exceeds that necessary for the activation of hydrogen in the gaseous state in the absence of a catalytic material.

It may be noted in passing that electrolytic reduction with metals possessing η values > 0.455 volt should be able to effect the reduction of substances which are not amenable to the catalytic process, further that no metal can possess an overpotential exceeding the value for which the energy exceeds that necessary for the desorption of atomic hydrogen or

$$\frac{96,540 \times 2}{4.2} \times \eta = 80,000 \text{ or } \eta = 1.80 \text{ volts.}$$

Metals having an η value less than 0.455 volt should show catalytic activity, since the adsorbed hydrogen will not be entirely immobilized; and the catalytic activity should increase with decreasing values in the overpotential. This can be seen from the following considerations:

Imagine a hydrogen molecule oscillating between two plane surfaces

¹ *Phil. Mag.*, 26, 1, 476 (1913).

situated parallel and close to one another, one plane surface being perfectly reflecting, and the other adsorbent. Every time the molecule strikes the reflecting surface it will be returned to the adsorbent one. Here it will oscillate in the field of attraction until sufficient time elapses for it to acquire energy by impact from other molecules or by radiation sufficient to permit of oscillation outside the range of attraction and regain the other surface when it will be reflected *de novo*. The alteration of the energy content of one molecule with the time is analogous to the energy distribution among a number of molecules at any given instant according to Maxwell's distribution law. It is evident that if the energy required for desorption is large, or the value of η high, the rate of interchange will be small, and the converse for substances possesses a small desorption energy. There is consequently a greater opportunity for two molecules of different reacting species to become adsorbed in juxtaposition to one another and so react than in the former case. Further, the rate of desorption or evaporation of the products of the reaction, which frequently governs the reaction rate, will be more rapid if the latent heat is small.

The following figures indicate how closely the catalytic activity in hydrogenation processes is related to the overpotential:

Metals in order of decreasing catalytic activity (Sabatier).

	Overpotential η volts.	
Nickel.....	0.03	—0.21
Cobalt.....	0.03	—0.01
Platinum.....	0.09	—0.01
Iron.....	0.08
Copper.....	0.36	—0.03

Palladium ($\eta = 0.23 - 0.46$ volt) has also a marked catalytic activity in certain hydrogen ion processes, while Dewar has shown that silver ($\eta = 0.05 - 0.15$ volt) occasionally exhibits extraordinary activity.

According to Sabatier, the following metals are inactive in catalytic hydrogenation processes.

Metal.	Overpotential η volts.
Tin.....	0.43 to 0.53
Lead.....	0.42 to 0.78
Mercury.....	0.35 to 0.64
Zinc.....	0.66 to 0.70

It will be noted that the figures given for the overpotentials fluctuate within somewhat wide limits; thus different samples of copper may give values within the ranges 0.03 and 0.36 volt. This fact is in perfect accord with our knowledge of the variation in catalytic activity of this metal. H. S. Taylor and the writer have shown that a sample of ordinary copper wire will only appreciably catalyze the combination of hydrogen

and oxygen at a temperature of 350° , while "active" copper produced by alternate oxidation and reduction is operative at 70° to 90° . Bright platinum ($\eta = 0.09$ volt) is ineffective for the oxidation of ammonia to nitric oxide, gray platinum ($\eta = 0.06$ volt) is extremely active, while black platinum ($\eta = 0.01$ volt) is found to be much too active for this conversion, nitrogen being formed in relatively large quantities.

Experiment has shown that in the case of copper also, there is a close relationship between catalytic activity and overpotential. It appears probable that these fluctuations in catalytic activity and overpotential in the same metal may be ascribed to the same cause, a difference in the surface structure of the metal. Under the microscope these differences are noted usually as a transition from a crystalline inactive variety to a powdery amorphous, occasionally microcrystalline active variety. The crystalline form may be converted into the active variety by a process of continued catalysis or by the continuous liberation of hydrogen at its surface. Metals deposited by a high current density are more active and possess a lower overpotential than those deposited under normal conditions, an indication that the elemental, cubic space lattice of the crystal is not so active as residues or fragments of the cubes from which one or more corners may be missing. In electro deposition the metallic ions tend to build up on the active form, and the same holds true for colloidal materials undergoing cataphoretic deposition. This gives an explanation, already proposed by Bancroft, for the formation of good deposits by such addition agents, and readily interprets Moller and Pring's observations¹ that a colloidal addition agent which lowered the surface tension of the electrolyte, and according to the bubble theory, should lower the overpotential also, actually raised it. The colloidal addition agent is deposited on the active areas of the electrode, leaving the less active areas exposed to function as the electrode, which consequently acquires a higher overpotential.

Sufficient data are not available to determine whether there is any relationship between the overpotential values and the quantity of colloid retained by the deposited metal. It might, however, be anticipated that metals exhibiting a high overvoltage or possessing a high latent heat of desorption for hydrogen would possess similar values for positively charged colloids, which on deposition would consequently not return so readily to the electrolyte. Mathers and Overman² state that 350 g. of peptone is adsorbed per ton of lead deposited from a perchlorate electrolyte or one g. of peptone will protect only 143 gram molecules of lead. Silver deposition certainly requires a far smaller quantity of protecting agent.

¹ *J. Chem. Soc.*, 105, 712 (1914).

² *Trans. Am. Electrochem. Soc.*, 13, 441 (1909).

In previous investigations it has been assumed that the energy required for the desorption of a product could be equated to the latent heat of evaporation. The above mentioned considerations however lead us to suppose that the latent heat of desorption is not equal to the latent heat of evaporation but varies with the nature of the surface from which the film is evaporating. On the radiation theory the latent heat of desorption per gram-molecule must be given by the equation, $E = Nh(\nu \text{ reactants} - \nu \text{ products})$, in which both metal and hydrogen must be included. The following preliminary considerations on this point are given with reserve since it is hoped to make the more exact analysis the subject of a future communication.

In the case of sublimation or even fusion, and vaporization when the melting and boiling point lie close together, according to Trouton's rule, the latent heat of change is proportional to the temperature at which that change of state takes place. The vibrational energy of the surface molecules at that temperature is approximately $3RT$ or the latent heat of change is proportional to the surface vibrational energy of molecules. If we assume that the energy for vaporization is supplied by radiation, the frequency of the radiation ν is given by the relationship

$$L = h\nu,$$

where L is the latent heat of sublimation and h , Planck's constant. It is generally assumed that in infra-red radiation the radiator is an atom; if we further assume that the frequency of the radiant energy and of the radiator are the same, then the frequency of the atom just before leaving the surface is ν and its kinetic energy is $\frac{1}{2}ma^2\nu^2$, where m is its mass and a the amplitude of vibration. The total kinetic and potential energy of the vibrating atom is therefore $ma^2\nu^2$ acquired by radiation $h\nu$, or $ma^2\nu^2 = h\nu$. It can easily be shown that this relationship is only a very approximate one, since it follows that T/ν , where ν is the vibration frequency of the surface molecule at the temperature of sublimation T should be constant.

An approximate value for this ratio for a number of elements is 2.5×10^{-10} . Exceptions are, however, very frequent, especially at very low or very high temperatures.

In the case under consideration the hydrogen molecule may be regarded as attached to neighboring metal atoms, atom to atom, and to oscillate with them but with different frequencies. The metal atoms vibrate with their natural frequency in the infra-red. The hydrogen molecule, however, although it can vibrate in the two directions parallel to the plane of the metal with its natural frequency, yet in the plane perpendicular to the metal surface has a frequency which is very different. At a certain distance from the metal surface there is a position of zero attraction for the hydrogen atoms. An atom approaching within this distance

will suffer a repulsion, while an atom receding from this point will undergo attraction until it passes outside the range of molecular action.¹ Each atom on the surface possesses a kinetic energy *per se*, the magnitude of which will, however, vary from instant to instant just as the number of atoms possessing different amounts of kinetic energy distributed in a collection of atoms at any given instant according to Maxwell's law of distribution, so the energy content of one atom must vary from second to second. The atoms consequently oscillate on the metal surface by virtue of their own kinetic energy, which appears as a damped vibrational movement under the influence of the attractive and repulsive forces; every now and then one atom or molecule acquires sufficient kinetic energy to vibrate outside the attraction zone of the metal and consequently is evaporated or desorbed. Thus from the latent heat of desorption it is possible to calculate the energy required to remove an atom from the position of zero attraction to a position outside of the range of molecular attraction. If this energy be supplied by radiation, then, assuming the conditions already referred to, it is possible to calculate both the amplitude and the vibration frequency of this forced vibration.

In the case of silver the mean value of the overpotential appears to be 0.10 volt \approx 0.05, giving an energy of desorption of 4,300 cal. per gram molecule or 3×10^{-13} ($\approx 1.5 \times 10^{-13}$) ergs per molecule. The average kinetic energy of a hydrogen molecule at 0° is 3.69×10^{-14} ergs. The energy of desorption is thus nearly 10 times that possessed by the molecule at that temperature. Assuming this energy to be acquired by infra-red radiation, then since $E = h\nu$

$$\nu = \frac{3 \times 10^{-13}}{6.55 \times 10^{-27}}; \text{ or } \nu = 4.6 \times 10^{13} (\approx 2.3 \times 10^{13})$$

being the vibration frequency of the hydrogen molecule and consequently that of each atom. We may regard the hydrogen atom and the adsorbing silver atom as vibrating identical distances with necessarily different frequencies. On equating the kinetic energies of the two masses,

$$ma^2\nu^2 = Ma^2\nu_1^2,$$

where m is the mass of the hydrogen atom, M the mass of the silver atom, a the amplitude of each atom, and ν and ν_1 their respective frequencies. The atomic weight of silver is 108, hence its vibrational frequency is

$$\nu_1 = \frac{4.6 \times 10^{13}}{\sqrt{108}} = 4.5 \times 10^{12}.$$

Lindemann's formula gives us a value of 4.36×10^{12} .

The mass of a hydrogen atom is 1.634×10^{-24} g., its energy in the adsorbed state is 1.5×10^{-13} ($\approx 0.75 \times 10^{-13}$) ergs, hence its velocity is

¹ Langmuir, *Phys. Rev.*, 8, 149 (1916).

3×10^8 ($\pm 1.5 \times 10^8$) cm. per second. If its vibration frequency is 4.6×10^{12} ($\pm 2.3 \times 10^{12}$) the average distance of travel, or average amplitude is v/ν or 0.8×10^{-8} cm. This must, therefore, be the range of molecular attraction beyond the nearest point of approach of the atom; the total distance calculated by other methods is approximately 2×10^{-8} cm.

In the following table are given the mean overpotentials of a number of elements, the energy of desorption in cal. per gram-molecule, $-\Delta U$, the vibration frequency of the adsorbed atom of hydrogen and that of the adsorbing metal calculated therefrom. The metal frequencies calculated from Lindemann's formula are given for comparison

Metal	Overpotential volts	ΔU	$\nu \times 10^{-12}$ Hydrogen	$\nu \times 10^{-12}$ Metal	$\nu \times 10^{-12}$ Metal calc (Lindemann)
Ag	0.10	4,300	4.6	4.5	4.36
Pt	0.08	3,600	4.1	3.0	4.36
Cu	0.13	5,800	6.13	7.6	6.7
Ni	0.12	5,200	5.6	7.5	8.2
Fe	0.08	3,600	3.96	5.3	8.3
Au	0.02	1,000	1.1	0.8	3.4
Pd*	0.23	10,250	11.0	10.9	5.7

* The heat of formation of "palladium hydride" is given as 500 cal. which, if correct, would correspondingly reduce the overpotential value.

In the metals given below, active hydrogen is the desorption product and no relationships obtain between the calculated values and those obtained from Lindemann's equation.

Hg	0.78	34,700	38.1	27	1.24
Zn	0.70	31,000	34.1	43	4.36
Sn	0.53	23,700	26.1	23	2.24
Cd	0.48	21,200	23.3	22	3.0

In spite of the great latitude in the overpotential values recorded and of the assumptions made as to the material nature of the radiator as well as to its independent oscillation in one plane, there is a rough agreement between the two values for the radiation frequencies. It is interesting to calculate these values for a hypothetical solid hydrogen electrode. Eucken¹ gives the latent heat of vaporization of hydrogen as 220 cal.; the latent heat of fusion may be taken as approximately equal to that of nitrogen, giving a latent heat of sublimation of 390 cal., the kinetic energy of the hydrogen molecule after desorption, viz., $3RT$ not being supplied by radiation. Hence to desorb hydrogen from a hydrogen electrode would require an overvoltage of only 0.009 volt and a corresponding radiation frequency of 4.30×10^{12} , a very close approximation to Lindemann's figure of 4.36×10^{12} .

¹ *Ber. Phys. Ges.*, 18, 4 (1916).

EXPERIMENTAL.

The Influence of Temperature on Overpotential.

In order to establish the conclusion that overpotential might be influenced by bubble size in elements possessing a small overpotential but not for those elements with a high value, experiments were conducted with electrodes of platinum, copper and zinc. MacInnes and Adler¹ showed that for overpotentials of the order of 0.001 to 0.002 volt there was a rough agreement between the observed bubble diameter and the calculated value. Owing, however, to the difficulties of measurement the error varied from 30 to 50%, it was clearly impossible so to refine their method for the very minute bubbles to be expected with high overpotential values. Accordingly attempts were made to determine the temperature coefficient of the overvoltage.

If the overvoltage is a simple function of the bubble size, then the temperature coefficient according to the relation, $96,540 \times 2 \times \eta = 3RT/\text{pr } \gamma$ is, $d\eta/dT = K(1/dT) + K\gamma$, where $K = 3R/\text{pr } 96,540 \times 2$, r being the bubble radius, p the gas pressure, and γ the surface tension.

The expression, $-T d\gamma/dT$, is equal to the latent heat of extension of the film, which in the case of water was found by Kelvin to be equal to half the work required to form the film, or $1/2\gamma$; hence $d\eta/dT = 1.5 K\gamma$, or $1.5 \eta/T$. Sheet metal electrodes were employed, each side 3.11 sq. cm in area. The electrodes were coated with a relatively thick film of electrolytically deposited metal and were subjected to the cathodic liberation of hydrogen in 0.1 N sulfuric acid for 48 hours before use. The overvoltages in 0.1 N sulfuric acid, maintained at suitable temperatures in a thermostat were determined by means of an auxiliary 0.1 N calomel electrode with acid of the same strength as the junction liquid, utilizing a Leeds and Northrup type of potentiometer. The potential of a hydrogen electrode, of the type suggested by G. N. Lewis, was determined under identical conditions. The overpotential was accordingly given by the relationship, $\eta_t = E/M_t - E/H_t$. E/M_t and E/H_t being the observed potential differences for the metal and the hydrogen electrodes at a temperature t . Errors due to liquid junction potentials and temperature differences were thus eliminated. The following values were obtained:

Metal	Current density Milliamps per sq. cm	Temperature, 25°	33°	43°	53°	63°
			Overvoltage in millivolts			
Platinum	1.6	5.5	1.5	0.5
	3.2	8.3	6.0	6.0	2.0	0.5
	4.8	10.8	11.0	5.2	3.0	3.3
	8.0	11.8	11.0	11.0	8.6	7.4
	10.4	15.8	15.6	12.7	11.0	9.1
	16.0	18.1	17.7	16.0	13.3	12.9

Mean value $d\eta/dT$ millivolts per degree . 0.13 0.19 0.23 0.13

Mean value obs. 0.17 millivolt per degree.

Calc. 0.053 millivolt per degree at 37°.

¹ THIS JOURNAL, 41, 200 (1919).

		Temperature, 20.5°.					
		30.5.	40.5.	50.5.	60.5.	67.	
Copper.....	1.6	103.4	71.2	37.1	12.7
	3.2	130.4	105.6	76.4	56.4	40.5	23.8
	4.8	150.4	121.9	93.4	73.4	56.5	41.5
	8.0	165.9	142.4	107.4	90.5	72.5	62.0
	10.4	166.9	147.4	107.9	98.5	79.0	73.0
	16.0	190.0	166.4	130.4	110.0	90.4
Mean value $\partial\eta/\partial T$ millivolts per degree...		2.5	3.3	1.9	1.8	1.5	
Mean value obs.....		2.2 millivolts per degree.					
Calc.....		0.5 millivolt per degree at 37°.					

		Temperature, 18°.			
		35	45.	55.	
Zinc...	1.6	655.0	654.0	655.9	653.1
	3.2	658.8	656.0	654.9	653.1
	4.8	665.4	658.7	654.9	655.1
	8.0	672.7	663.7	655.9	661.1
	10.4	679.2	665.7	656.9	661.1
	16.0	680.0	672.2	658.9	663.0
Mean value $\partial\eta/\partial T$ millivolts per degree..		0.40	0.54	0.0	
Mean value obs.....		0.31 millivolt per degree.			
Calc.....		3.2 millivolts per degree at 37°.			

It will be noted that in the case of zinc there is no relationship between the observed and calculated potential temperature decrement, the total variation over nearly 40° being only 2%. In the case of copper and platinum a definite temperature coefficient is observed which, however, is considerably greater than the calculated value, although in the case of copper its variation with the temperature is as would be expected on the basis of the bubble theory. The large value of the coefficient must in part be attributed to the greater mobility (at the higher temperatures) of the hydrogen molecules attached to the surface, permitting the formation of larger bubbles, and also to the increased diffusion rate of the dissolved hydrogen from the electrode surface permitting a greater evaporation rate, with a consequent increase in the current density before the maximum value of the overpotential is obtained. The following calculation gives an approximation to the ratios of the current densities required for the metals before the overpotential reaches a maximum. The latent heats of desorption of hydrogen from platinum, copper and zinc are, respectively, 3,600, 5,800 and 31,000 cal. per mol. The number of molecules possessing sufficient energy to leave the surface at any time is given by the relation $N_s/N = e^{-\frac{Q}{RT}}$, where N_s molecules out of N molecules are capable of evaporating.

For a temperature of 300° K. we find that one molecule in $10^{3.6}$ for platinum, one in $10^{4.2}$ for copper and one in 10^{23} for zinc are capable of evaporation. No data appear available to determine the absolute rates of evaporation under these conditions. It may be noted that as one sq. cm. of surface will adsorb 6×10^{14} molecules while a milliampere will de-

posit $3 \cdot 10^{15}$ molecules per second, evaporation must, therefore, be relatively rapid. In any case, although the absolute rates are unknown, the relative evaporation rates give us a measure of the relative current densities necessary to keep the surface permanently covered with hydrogen, the condition for the occurrence of the maximum overpotential effect. The figures given above indicate that small currents polarize zinc much more easily than copper or platinum.

Overpotential and Electrode Surface.

The alteration of the overpotential with the nature of the surface is well marked in the case of platinum and, according to the previous discussion, the same should hold true for all catalytically active metals. The following figures illustrate the magnitude of these changes in the cases of copper and zinc.

An electrolytic copper electrode was made the cathode in a 0.1 *N* sulfuric acid solution, hydrogen being continuously and rapidly disengaged at its surface, the overpotential being determined from time to time. It was found that there was a continuous fall in the η value and the bright crystalline appearance of the metal was replaced by a honeycomb-like amorphous layer occasionally yellowish brown in appearance. The observed values were as follows

	Time Hours	Overvoltage, η [8 milliamperes per sq. cm.] v.	Appearance
Temp. 20.5°	0	0.364	microcrystalline, bright
	24	0.284	reddish
	48	0.178	brownish, amorphous
	56	0.166	brownish, amorphous

It would appear possible to reduce the overpotential of copper to the lowest figure recorded, *viz.*, 0.03 volt by continued treatment. At higher temperatures this change takes place somewhat more rapidly, at least in the earlier stages.

	Time Hours	Overvoltage, η [8 milliamperes per sq. cm.] v.
Temp. 55°	0	0.341
	1	0.208
	2	0.178
	3	0.169
	5	0.161

Very spongy copper deposited by high current densities will, if opportunity be given for the occluded hydrogen to escape, rapidly acquire a relatively low overpotential.

	Time, Hours	Overvoltage, η [8 milli- amperes per sq. cm.]
Temp. 20.5°	0	0.325
	3	0.140
	5	0.139

In the case of zinc these differences in overvoltage are much less marked as will be noted from the following figures:

Time. Hours	Overvoltage. 8 milli- amperes per sq cm	Appearance
0	0.841	bright, metallic crystalline
15	0.727	slightly dull
48	0.673	distinctly gray

Catalytic Activity and Overpotential.

A small strip of copper was alternately oxidized and reduced by hydrogen until it began to show signs of catalytic activity toward a hydrogen-oxygen mixture. The temperature at which traces of water were being formed, which frequently coincided with the appearance of changing oxide films on the metal surface, was noted, the metal being then removed and placed in the cell for the determination of its overpotential. Although as a result of a number of experiments no direct relationship between the overpotential and the temperature of apparent catalytic activity could be found, yet in all cases the overpotential fell with the temperature, or with the increase of catalytic activity, as will be noted from the following figures:

Temperature of catalysis Degrees	Overpotential Volts
300	0.362
280	0.353
260	0.328
250	0.306
230	0.238
150	0.195

It would appear, however, that the fraction of the total surface which has to be operative to reduce sensibly the overpotential is much greater than that necessary to effect an appreciable difference in catalytic activity, indicating that the metallic catalysts as ordinarily prepared are comparatively inefficient and should be capable of great improvement.

Summary.

It is suggested that overpotential is a measure of the energy required for the desorption of hydrogen from a metallic surface.

Metals with low latent heats of desorption are catalytically active, the activity increasing with decreasing overpotentials. Metals with overpotentials exceeding 0.455 volt are catalytically inert and no metal can possess an overvoltage exceeding 1.80 volts.

The calculated values of the catalytic activities of the metals are in agreement with Sabatier's qualitative observations.

A tentative suggestion for the mechanism of the process of desorption on the radiation hypothesis is advanced.

УВЕНА, ВЪПРОС.

NOTES.

Correction.—Lieut. E. B. Vliet has called our attention to a number of errors in the numbers appearing in the last column (headed “% deviation”) of Tables I and III of the paper on the General Boiling Point Law in the May JOURNAL (pp. 732 and 735). In Table I, the first number should read 1.45 instead of 0.24. In Table III the numbers given in the last column should be stricken out. The corrected values may readily be computed from the data in the two preceding columns. The foregoing corrections do not affect the remainder of the paper in any essential respect.

EDWARD W. WASHBURN AND JOHN W. READ.

Correction.—In the recent paper by Keyes and Felsing¹ on “The Equation of State for Liquids and Vapors. I. The Vapor Phase of Ethyl Ether,” the following corrections should be made:

P. 594: Equation 5 should read

$$p = \frac{R_z T}{v - \delta_z} - \frac{A_z}{(v - l_z)^2}.$$

P. 597: 3rd paragraph, middle of page. 2nd sentence, replace “Equation 2” by “Equation 1,” and insert “scale” between “no” and “corrections” immediately following.

P. 597: footnote 3, omit the last sentence, beginning “Strictly . . .”

P. 610: Table II. The columns should be headed, beginning with the second column

$$\delta, \delta, \frac{R}{v - \delta}, \frac{R}{v - \delta}, \phi, \phi.$$

P. 611: Third sentence on the page reading “The equation. . . .” change e to l and change corrections to correctness.

P. 611: In Table III change the number 7058.6 in the pressure equation to 7050.6

P. 618: In Table VI set $2\beta_2 = 6.1748 \equiv 6.216 = \beta_1$ instead of $2\beta_2 = 6.748 \equiv 6.216 = \beta_1$.

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¹ THIS JOURNAL, 41, 589 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

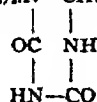
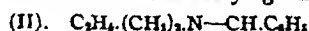
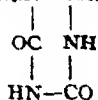
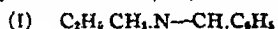
FOUR-MEMBERED CYCLIC UREAS. III. THE CONDENSATION OF ISOCYANIC ACID WITH ALKYL SCHIFF BASES AND RELATED COMPOUNDS.¹

BY WILLIAM J. HALE AND NORBERT A. LANGE.

Received September 6, 1919.

In our previous communication² attention was drawn to the fact that the addition of isocyanic acid to a Schiff base, where an ethyl group was attached to a nitrogen of the —N:C complex, resulted in the formation of a diketocyanidine. Two molecules of isocyanic acid were found to enter into condensation with one molecule of Schiff base. The reaction is exactly analogous to the polymerization of isocyanic acid to cyanuric acid and finds its counterpart in the work of Staudinger,³ who showed that two molecules of isocyanic acid condense in similar fashion with one molecule of a ketene.

For the further study of this reaction just mentioned, we have prepared the benzylidene derivatives of 3 normal primary alkyl amines by condensation of the latter with benzaldehyde. These alkyl Schiff bases were made thus to condense with isocyanic acid and to yield the expected triazines; from benzylidene propylamine, 1-propyl-6-phenyl-2,4-diketohexahydrocyanidine (I); from benzylidene butylamine, the corresponding 1-butyl derivative (II); and from benzylidene amylamine, the corresponding 1-amyl derivative (III). When, on the other hand an aryl group is at-



tached to the nitrogen of the —N:C complex of a Schiff base we have shown that the base now reacts with only one molecule of isocyanic acid to the production of a 4-membered cyclic urea or uretidone (see Papers I and II of this series).⁴ The reaction is now being studied in more detail.

¹ The work described in this article forms part of a thesis submitted by Norbert A. Lange, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

² THIS JOURNAL, 41, 379 (1919).

³ *Ann.*, 374, 11 (1911); *Ber.*, 50, 1042 (1917).

⁴ THIS JOURNAL, 41, 370, 379 (1919).

We have thought now to apply this study to other compounds containing the —N : C : complex or, as we shall call it, the carbimino nucleus. With Schiff bases the nitrogen of this nucleus is attached directly to an alkyl or aryl group. We have endeavored to condense isocyanic acid with compounds containing this carbimino nucleus where the nitrogen is attached to amino derivatives. For example, the compounds benzyldene-phenylhydrazine, $(\text{C}_6\text{H}_5.\text{CH} : \text{N.NH}.\text{C}_6\text{H}_5)$, benzyldene *as*-diphenylhydrazine, $(\text{C}_6\text{H}_5.\text{CH} : \text{N.N}(\text{C}_6\text{H}_5)_2)$, and also benzyldene-benzylhydrazine, $(\text{C}_6\text{H}_5.\text{CH} : \text{N.NH}.\text{CH}_2.\text{C}_6\text{H}_5)$, were each investigated in this direction. Of these compounds neither the first nor second showed any tendency to add cyanic acid at low temperature and in glacial acetic acid solution. The first, however, is reported¹ as adding phenyl-isocyanate to the imino position during warming to 170° after the manner of the Wöhler synthesis, producing 1-benzyldene-2,4-diphenyl-semicarbazone. The imino hydrogen in the last named of the 3 semicarbazone compounds offers indeed a ready point of attack for isocyanic acid itself, as has just recently been demonstrated by Bailey and Moore,² and the products resulting, or 1-benzyldene-2-benzyl-semicarbazone, $(\text{C}_6\text{H}_5.\text{CH} : \text{N.N}(\text{CONH}_2).\text{CH}_2.\text{C}_6\text{H}_5)$, no longer is able to add isocyanic acid. This general type of condensation of isocyanic acid with imino hydrogen has been investigated in detail by Busch and Walter³ and by Bailey and Read.⁴ It would seem possible to effect the addition of isocyanic acid to a di-substituted N-amino derivative of the carbimino nucleus (*i. e.*, to the type $\text{R}_2\text{N—N : CHR}$) but more than likely phenyl isocyanate or other ethers of this acid will constitute the proper means of attack. Bailey and Moore already have reported the addition of isocyanic acid to benzalazine, a compound possessing two carbimino nuclei $(\text{C}_6\text{H}_5.\text{CH} : \text{N : N : CH}.\text{C}_6\text{H}_5)$.

Though the work of these authors cannot at this time be discussed in detail, it has seemed advisable to us to investigate this tendency for imino hydrogen on the one hand and the carbimino nucleus on the other to enter into condensation with isocyanic acid. Thus, as just stated, Bailey and Moore prepared 1-benzyldene-2-benzyl-semicarbazone (V) by the action of isocyanic acid upon benzyldene-benzylhydrazine. Their description of the work, however, coupled with the statement that the product did not undergo hydrolysis when subjected to distillation with steam in the presence of a small amount of sulfuric acid raised considerable doubt in our minds as to the exact manner in which the isocyanic acid had attached itself. From our earlier publication it may be

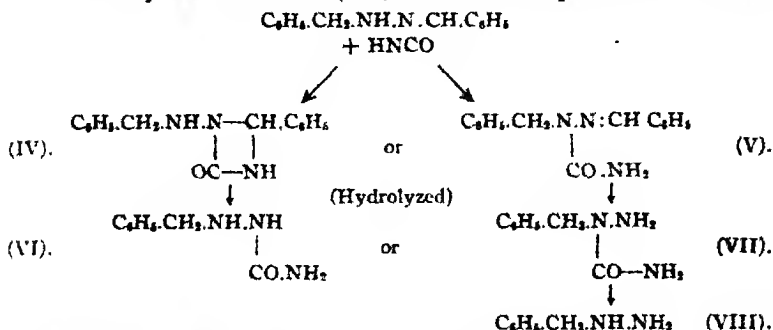
¹ Busch and Walter, *Ber.*, 36, 1360 (1903).

² *THIS JOURNAL*, 39, 290 (1917).

³ *Ber.*, 36, 1359 (1903).

⁴ *THIS JOURNAL*, 37, 935 (1915).

inferred that isocyanic acid could add directly to the carbimino nucleus and result in a compound of structure (IV). If, on the other hand, the attack took place on the imino hydrogen we should obtain the compound V as reported by Bailey and Moore. In either case the product should be capable of hydrolysis with liberation of benzaldehyde and a semicarbazide, 1-benzyl-semicarbazide (VI) if from a compound of Formula IV and 2-benzyl-semicarbazide (VII) if from a compound of Formula V.



The semicarbazides (VI) and (VII) have both been reported in the literature. The first (VI) was prepared by Kessler and Rupe¹ by the reduction of benzylidene-semicarbazone ($\text{C}_6\text{H}_5\text{CH:N.NH.CO.NH}_2$) through the action of sodium amalgam and alcohol. The pure product melts at 155° and its hydrochloride at $178\text{--}180^\circ$. The second (VII) was prepared by Curtius² through the action of isocyanic acid upon benzylhydrazine. The compound which Curtius obtained melted not sharply at 135° . He assigned to it the formula of a 1-benzyl-semicarbazide (identical with VI). Its strong basic properties, however, led Busch, Opfermann and Walther³ to identify it as a 2-benzyl-semicarbazide (VII), which they reported as melting at $127\text{--}128^\circ$. Later the work of Kessler and Rupe⁴ eliminated all possibility of the Curtius formula for this compound in that they actually prepared the 1-benzyl-semicarbazide (see above) whose properties in no wise tallied with those reported by Curtius. We must conclude, therefore, that isocyanic acid attacks preferably the imino hydrogen in benzylhydrazine (*i. e.*, at the α -nitrogen position). This has appeared to be a general conclusion for alkyl hydrazines, but for aryl hydrazines the β -position (*i. e.*, the amino hydrogen) affords also a likely point of attack, the more stable type of compound thus resulting. If, as is common, the α -position is first attacked the more or less labile product may be transformed by gentle heat into the stable

¹ *Ber.*, 43, 26 (1912).

² *J. prakt. Chem.*, [2] 62, 97 (1900).

³ *Ber.*, 37, 2325 (1904).

⁴ *Loc. cit.*

β -form. According to Busch, Opfermann and Walther,¹ if a benzoyl hydrazine is subjected to the action of mustard oil or an alkyl isocyanate this strongly negative aroyl group forces the point of attack altogether upon the β -nitrogen position. The distinctly active character of the imino hydrogen as against the amino hydrogen may further be seen in the action of chloroacetic acid upon hydrazino-acetic acid ($\text{H}_2\text{N.NH.CH}_2\text{COOH}$) to give hydrazinodiacetic acid ($\text{H}_2\text{N.N}(\text{CH}_2\text{COOH})_2$).² Phenylhydrazine and chloroacetic acid react similarly to give *as*-phenylhydrazinoacetic acid ($\text{H}_2\text{N.N}(\text{C}_6\text{H}_5)\text{CH}_2\text{COOH}$).

From the consideration just stated we may easily interpret the action of isocyanic acid upon benzylhydrazine as attacking the α -nitrogen position and leading to 2-benzyl-semicarbazide as reported by Busch *et al.* No statement, however, is made by these authors as to the possibility of transforming their 2-benzyl-semicarbazide into a 1-benzyl-semicarbazide. Their general rule indeed would seem to eliminate this possibility in that they state that methyl- or benzylhydrazine takes up mustard oil or alkyl isocyanates exclusively upon the α -nitrogen and the resulting 2,4-substituted compound (*e. g.*, $\text{C}_6\text{H}_5\text{NH.CO.N}(\text{CH}_2\text{C}_6\text{H}_5)_2$) does not suffer transformation into the 1,4-substituted compound (*e. g.*, $\text{C}_6\text{H}_5\text{NH.CO.NH.NH.CH}_2\text{C}_6\text{H}_5$). In such examples as phenyl-isocyanate upon phenylhydrazine the 1,4-type of compound above results as may be gathered from one of the preceding statements.³ In our experiments upon the 2-benzyl-semicarbazide of Curtius and also Busch, *et al.*, we now find that a transformation of this carbazide into the 1,4-substituted form (*i. e.*, 1-benzyl-semicarbazide) takes place simply upon melting of the former. In those cases where allyl isocyanates were employed by Busch, *et al.*, it may be assumed that the alkyl radical in the carbamino group affords greater stability to the molecule with the lack of any tendency to suffer this transformation. We prepared the 2-benzyl-semicarbazide by carefully adding potassium cyanate to a cold aqueous solution of benzylhydrazine hydrochloride. The crystalline product thus separating was dried *in vacuo* and found to melt between 130° and 135° . The slight solubility of 1-benzyl-semicarbazide in cold chloroform and the ready solubility in this same solvent of the greater part of this product melting at 130 – 35° offered a simple means for the separation of the two semicarbazides. That part of this 130 – 35° product which could be taken up in cold chloroform was immediately precipitated therefrom, by the addition of ligroin, in small flattened prisms melting at 135 – 6° . The minute portion remaining undissolved by the chloroform consisted chiefly of the higher melting

¹ *Loc. cit.*, p. 2330.

² *J. prakt. Chem.*, [2] 83, 271 (1911); *THIS JOURNAL*, 36, 1747 (1914).

³ *Ber.*, 36, 1362 (1903).

semicarbazide, but its presence was just sufficient to render difficult any attempts to determine the correct melting point of the 130–35° product. Curtius, however, possibly by repeated and careful crystallizations, actually isolated the pure compound (m. p. 135°), whereas Busch, Oppermann and Walther undoubtedly had a compound slightly contaminated with a little of the 1-benzyl-semicarbazide and hence the lower and inexact melting point, 127–8°.

When condensed with benzaldehyde at ordinary temperatures the pure 2-benzyl-semicarbazide yielded the well known 1-benzylidene-2-benzyl-semicarbazone (V) melting at 155.5°, the same compound as reported by Busch *et al.*, but with slightly lower melting point (153–154°). When the 2-benzyl-semicarbazide was melted and the cooled product crystallized from alcohol beautiful, glistening leaflets of 1-benzyl-semicarbazide, melting at 155–6°, were obtained. This final product was now shown to be identical with the 1-benzyl-semicarbazide prepared by Kessler and Rupe;¹ its hydrochloride also, both when alone and when mixed with samples of the hydrochloride of the compound prepared by Kessler and Rupe, melted at the recorded point 178–180°. There remains, therefore, no further question concerning the transformation of 2-benzyl-semicarbazide into 1-benzyl-semicarbazide at the point of fusion of the former. This transformation was, of course, accomplished in the case of the pure product (m. p. 135–6°) as well as for the more or less impure mixture which one first obtains in the action of isocyanic acid upon benzylhydrazine (130–135°). Any chance that the two semicarbazides might have been formed simultaneously is thus eliminated.

With the matter thus cleared concerning the structure and isolation of 2-benzyl- and 1-benzyl-semicarbazides (VII and VI), we saw at once the impossibility of proving anything concerning the structure of that addition product of isocyanic acid upon benzylidene-benzylhydrazone. Through the negative results obtained by us in our attempts to acetylate this addition product we were forced to the conclusion that a cyclic urea structure as a uretidone (shown in IV) cannot likely be present. In our earlier work we have remarked on the ease with which this latter type of compound undergoes acetylation. Further than this we may consider the hydrolysis which the compound suffers as not sufficiently speedy to indicate the presence of a uretidone.

The hydrolysis of the addition product (now to be considered as of structure V) as carried out by Bailey and Moore, was accompanied by a slight oxidation in the presence of sulfuric acid and neither benzaldehyde nor other products could be detected. We accomplished the hydrolysis by mixing the compound with dil. hydrochloric acid and subjecting this mixture to distillation with steam. The requisite quantity of benzalde-

¹ *Loc. cit.*

hyde (1 mol.) is slowly liberated during long boiling, and the contents of the flask, upon evaporation and recrystallization from alcohol gave a product melting at 110°. As it proved not to be the 2-benzyl-semicarbazide (VII) which we anticipated we had only to look to the slight loss in carbon dioxide and ammonia during the distillation to anticipate yet another hydrolytic step with the final product easy of identification—that of benzylhydrazine (VIII) in the form of its hydrochloride. A slight contamination of this hydrochloride with a dihydrochloride was noted; the latter is removed by its lesser degree of solubility in absolute alcohol. Pure benzylhydrazine hydrochloride is reported to melt at 111°. The pure product and that obtained by us when mixed melt at 110–11°. We identified our product conclusively by causing it to react with isocyanic acid in aqueous solution. The product of course proved to be 2-benzyl-semicarbazide (VII), m. p. 135–36°.

The addition of isocyanic acid to benzylidene-benzylhydrazone is, therefore, to be interpreted in accordance with Formula V, which Bailey and Moore have proposed. The hydrolysis of this 1-benzylidene-2-benzyl-semicarbazone, however, is now seen to be possible and through its study we have come to a clear understanding concerning the stability of 1-benzyl-semicarbazide over that of the corresponding 2-benzyl-semicarbazide. The tendency of isocyanic acid to select an imino or amino hydrogen in hydrazino derivatives is more and more clearly shown to depend upon the nature of the substituents on the nitrogen atoms of the hydrazines; the more strongly negative substituents force the attack to the β -nitrogen position. In the case of individual amino derivatives a primary amine naturally takes preference over a secondary amine when open to action with isocyanic acid. In the carbimino nucleus again we note the great influence of a substituent either upon the nitrogen or upon the carbon atoms in directing the action of isocyanic acid. With an alkyl substituent upon the nitrogen atom only ketocyanidines result. When an aryl group is attached to the nitrogen atom only the uretidone is produced. None of these condensations, however, is likely to proceed when a simple amino group is attached to the nitrogen atom; no matter whether the hydrogen atoms of the amino group are entirely replaced by aryl groups as seen above in the case of benzylidene-*as*-diphenylhydrazone, or only one of the hydrogen atoms is so substituted, as in benzylidene-phenylhydrazone. The conditions which will make for a uretidone formation from a carbimino nucleus even when the nitrogen is attached to amino derivatives are now under investigation.

Experimental Part.

The alkyl Schiff bases employed in this work were prepared by adding an equimolecular quantity of benzaldehyde to the alkyl amine in ques-

tion (*n*-propyl, *n*-butyl, and *n*-amyl) at 5–10° and drying the product over anhydrous potassium carbonate.

1 - Propyl - 6 - phenyl - 2,4 - diketo-hexahydrocyanidine, $C_8H_7 \cdot C_6H_5O_2N_2 \cdot C_3H_7$ (I).—To a well-cooled solution of benzylidene-*n*-propylamine in glacial acetic acid is slowly added, during constant stirring, small quantities of potassium cyanate until a slight excess over two molecules have been used. The mixture is then set aside in a cool place for several days, after which it is transferred to a flask containing water and a few cubic centimeters of hydrochloric acid and subjected to distillation with steam. When no further trace of benzaldehyde is detectable in the distillate the solution in the flask is filtered, evaporated to small volume and then allowed to stand; crystals of the cyanidine derivative are soon deposited. Several crystallizations from alcohol gave fine, colorless, flaky needles melting at 211°. This propyl-phenyl-diketocyanidine is readily soluble in acetic acid; fairly soluble in alcohol, chloroform, acetone, ethyl acetate; slightly soluble in ether, benzene or water; and insoluble in ligroin. The solubilities partake closely after those of the corresponding ethyl derivative as reported in the previous publication.¹ The ethyl derivative is also slightly soluble in benzene—a point of correction for the description given in the earlier paper.

Calc. for $C_{11}H_{11}O_2N_2$: C, 61.77; H, 6.48, N, 18.03 Found. C, 61.76; H, 6.58; N, 18.38.

1 - Propyl - 6 - phenyl - 1 - acetyl - 2,4 - diketo - hexahydrocyanidine, $C_8H_7 \cdot C_6H_5O_2N_2 \cdot (COCH_3) \cdot C_3H_7$.—When the propyl-phenyl-diketocyanidine obtained above is boiled for a few minutes with acetic anhydride and fused sodium acetate and the mixture poured upon ice a crystalline mono-acetyl derivative is readily obtained. The compound may be purified by crystallization from 80% alcohol. The small colorless prisms melt at 120°. It is readily soluble in almost all of the organic solvents; only fairly soluble in ligroin and insoluble in water. The determination of percentage of carbon and hydrogen could not lead to definite conclusions. A nitrogen determination, however, sufficed to show the presence of only one acetyl group, more than likely in the 3-position.

Calc. for $C_{12}H_{13}O_2N_2$: N, 15.27 Found: 15.43.

1 - Butyl - 6 - phenyl - 2,4 - diketo - hexahydrocyanidine, $C_8H_7 \cdot C_6H_5O_2N_2 \cdot C_4H_9$ (II).—Benzylidene-*n*-butylamine was digested with potassium cyanate in a cold glacial acetic acid solution in exactly analogous manner to that described above for the preparation of propyl-phenyl-diketocyanidine. The final crystalline product crystallized from alcohol melts at 188°. It is readily soluble in acetic acid; fairly soluble in alcohol, chloroform, acetone, ethyl acetate; slightly soluble in ether, benzene, or water; and insoluble in ligroin.

¹ *Loc. cit.*

The preparation of acetyl derivatives was not undertaken either here or in the succeeding case, as one instance seemed sufficient to establish the constitutions proposed.

Calc. for $C_{10}H_{17}O_2N_2$: C, 63.13; H, 6.93, N, 17.00. Found: C, 63.41; H, 7.03; N, 17.10.

1 - Amyl - 6 - phenyl - 2,4 - diketo - hexahydrocyanidine, $C_8H_{11}-C_6H_5O_2N_2.C_4H_9$ (III).—Benzylidene-*n*-amylamine was here digested with potassium cyanate in cold, glacial, acetic acid solution and the operation carried out exactly as described for the two preceding ketocyanidines. Amyl-phenyl-diketocyanidine was purified by crystallization from alcohol and melts at 202° . It is readily soluble in acetic acid, chloroform or acetone; fairly soluble in alcohol or ethyl acetate; slightly soluble in ether, benzene or water, and insoluble in ligroin.

Calc. for $C_{14}H_{19}O_2N_2$: C, 64.34; H, 7.33, N, 16.09. Found: C, 64.49; H, 7.43; N, 16.37.

Hydrolysis of 1 - benzylidene - 2 - benzyl - semicarbazone, $C_6H_5-CH_2.N(CO.NH_2).N-CH.C_6H_5$.—This compound was prepared according to the directions of Bailey and Moore¹ by first reducing benzalazine with sodium amalgam and then treating the reduced product, benzylidene-benzylhydrazone, with potassium cyanate in cold, glacial, acetic acid solution. The substance thus separating out may be crystallized from ether and melts at 155.5° , or practically 156° , as reported by Bailey and Moore. It is readily soluble in most organic solvents, but only slightly soluble in ligroin. When placed in a flask containing a little water and hydrochloric acid and subjected to distillation with steam the product is slowly hydrolyzed. This process was continued until the distillate no longer contained benzaldehyde, after which the contents of the flask was filtered and finally evaporated to dryness upon a water bath. The dry residue was next boiled with a small amount of absolute alcohol and the clear filtrate from the insoluble portion (the dihydrochloride of benzylhydrazine), allowed to stand. The crystals of benzylhydrazine hydrochloride appeared in glistening leaflets melting at 110° . Pure benzylhydrazine hydrochloride melts at 111° ; a mixture of the latter and the sample we obtained in the hydrolysis melted at $110-11^\circ$. In all respects the hydrolytic product checked with the properties of pure benzylhydrazine hydrochloride. The hydrolysis, therefore, may be interpreted as proceeding in the manner previously indicated, (V) \rightarrow (VII) \rightarrow (VIII).

When the final hydrolytic product (*i. e.*, the benzylhydrazine hydrochloride) was dissolved in a very small amount of water and a little more than an equimolecular quantity of potassium cyanate added to the solution there precipitated, after a short time, colorless crystals melting at $130-35^\circ$, and thus in agreement with the results found by Busch *et al.*,¹

¹ *Loc. cit.*

when isocyanic acid was allowed to condense with benzylhydrazine to give 2-benzyl-semicarbazide (m. p. $135-36^{\circ}$). A sample prepared according to the method of Busch *et al.*, melted at $130-35^{\circ}$, and when mixed with our product above the mixture likewise melted at $130-35^{\circ}$. There would seem to be no doubt concerning the identity of the two compounds—that prepared according to Busch and that obtained by the action of isocyanic acid upon the hydrolytic product.

Calc. for $C_8H_{11}ON_3$: C, 58.15; H, 6.71; N, 25.45 Found: C, 58.39; H, 6.87; N, 25.23.

Preparation of Pure 2 - Benzyl - semicarbazide, $C_6H_5.CH_2N(NH_2).CO.NH_2$ (VII).—The action of potassium cyanate upon an aqueous solution of benzylhydrazine is reported by Curtius¹ to give a 1-benzyl-semicarbazide melting at 135° . The product of this same reaction as carried out by Busch, Opfermann and Walther¹ is construed as a 2-benzyl-semicarbazide melting at $127-28^{\circ}$. Kessler and Rupe¹ prepared the pure 1-benzyl-semicarbazide (m. p. 155°) as described in our theoretical considerations. When potassium cyanate is added to an ice-cold concentrated aqueous solution of benzylhydrazine (in equimolecular quantities), the crystals of 2-benzyl-semicarbazide are at once precipitated. Filtered off and dried *in vacuo* the product melts at $126-135^{\circ}$. These crystals are now mixed with ice-cold chloroform and the mixture filtered immediately by suction, pouring a little chloroform also upon the filter to insure removal of last traces of the soluble material. Upon the addition of ligroin to this chloroform filtrate small glistening colorless flat prisms of 2-benzyl-semicarbazide appear. The product may be again taken up in chloroform and precipitated by ligroin, but the melting point is not changed— $135-36^{\circ}$. 2-Benzyl-semicarbazide is readily soluble in alcohol, acetone, chloroform, ethyl acetate or glacial acetic acid; fairly soluble in benzene or water; slightly soluble in ether; and insoluble in ligroin. This semicarbazide does not reduce Fehling's solution in the cold, even after several days' standing, but upon warming the reduction is accomplished slowly. At the temperature of its melting point it is transformed into 1-benzyl-semicarbazide.

Preparation of 1 - Benzyl - semicarbazide, $C_6H_5.CH_2.NH.NH.CO.NH_2$ (VI).—When 2 benzyl-semicarbazide is heated in an air bath to the point of melting for a few minutes and the cooled product then crystallized from 20% alcohol, colorless prisms of 1-benzyl-semicarbazide are obtained. These crystals are not so flattened nor so small as those of 2-benzyl-semicarbazide. Both the melting point (155°) and the physical properties of this product are identical with that compound prepared by Kessler and Rupe. 1-Benzyl-semicarbazide is readily soluble in alcohol, acetone or glacial acetic acid; fairly soluble in chloroform, ethyl acetate,

¹ *Loc. cit.*

or water; slightly soluble in benzene or ether; and insoluble in ligroin. These solubilities differ somewhat from those of the 2-benzyl-semicarbazide. In cold chloroform very little of the product dissolves and hence a means of separating the two semicarbazides is afforded. This semicarbazide begins to reduce Fehling's solution even in the cold and reduces it readily upon warming, as recorded by Busch *et al.* A sample of this semicarbazide and an equal quantity of 2-benzyl-semicarbazide melted as low as $120-4^{\circ}$, hence an explanation of the indefinite results obtained by other investigators.

Action of Isocyanic Acid upon N-Amino Derivatives of Carbimino Nucleus.

As previously stated, the compounds here subjected to the action of isocyanic acid failed to condense with the latter at low temperatures either in glacial acetic or propionic acid. Benzylidene-*as*-diphenylhydrazone ($C_6H_5.CH : N.N : (C_6H_5)_2$) was brought into reaction under these conditions and also in a mixture of benzene and acetic acid in order to increase somewhat its solubility. No reaction could be detected. In a similar manner benzylidene-phenylhydrazone ($C_6H_5.CH : N.NH.C_6H_5$) was found to be unreactive toward isocyanic acid, but as discussed in our theoretical considerations, this compound does condense with phenyl isocyanate at high temperature. 1-Benzylidene-2-benzyl-semicarbazone as also previously discussed, failed to condense further with isocyanic acid. Though the carbimino nucleus is a favored complex for condensation with isocyanic acid, we note further that certain substituents on the nitrogen atom may considerably retard this tendency for condensation.

MIDLAND, MICH

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,
U. S. DEPARTMENT OF AGRICULTURE.]

THE OCCURRENCE OF MELEZITOSE IN HONEY.

By C. S. HUDSON AND S. F. SHERWOOD

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We recently¹ called attention to the abundant occurrence of the rare trisaccharide melezitose in a manna that forms upon Douglas fir trees in British Columbia during summer droughts. Since bees often collect manna and honey-dew in times of drought when the preferred floral nectar is scarce it would appear to be possible that honey from the particular region of British Columbia where this Douglas fir manna occurs would contain melezitose. An occurrence of melezitose in honey would not only be of general scientific interest but would require the attention of the food analyst because melezitose may readily be confused with cane sugar,

¹ THIS JOURNAL, 40, 1456-60 (1918).

one of the recognized adulterants of honey. While we were discussing this matter along these lines and were planning to obtain honey from the wilds of British Columbia there came an answer to the question in a most unexpected way. A sample of honey was received from central Pennsylvania, accompanied by a statement that it had proved unfit winter food for bees and a request that a chemical analysis be made in the hope of disclosing why the bees had died. Bees do not winter well upon honey-dew honey in general, as they seem unable to digest or assimilate such honey fully; but this material had caused even more difficulty than ordinary honey-dew honey. This sample of honey had thoroughly crystallized in the comb and the appearance of the crystals was different from that of *d*-glucose, the sugar that frequently crystallizes from honey. It was soon determined that the crystals were pure *melezitose*.¹ Subsequently we have obtained samples of comb honey from two localities in Maryland, near the District of Columbia, one produced in 1917, and the other in 1918, both of which also contain much melezitose in crystalline form. The sample from Pennsylvania was from the crop of 1917, and in the summer of 1918 similar honey, rich in crystalline melezitose, was produced in the same locality. It can hardly be doubted, therefore, that melezitose occurs not infrequently in honey, and it seems indeed remarkable that its crystals, which can be readily distinguished from those of glucose, have never before been observed in honey. We have at least not been able to find any record of such an observation in the extensive literature that deals with the composition of honey. The mode of origin of the three samples of honey that have been found to contain melezitose will be described after the presentation of the chemical data on the identification of the sugar.

Identification of Melezitose in Three Samples of Honey.

Comb Honey from Port Royal, Juniata County, Pennsylvania.—In one section of this honey the contents of 90% of the cells had crystallized thoroughly and solid masses having the shape of the cells could be removed from the wax of the comb. In two other sections the crystallization was slightly less pronounced. A quantity of the honey was removed mechanically with a knife blade from the wax, ground in a mortar with glacial acetic acid, which is miscible with the sirupy portion of honey but does not dissolve crystalline melezitose or glucose, and the crystals were separated from the liquid by filtration. They were washed with glacial acetic acid, then with absolute alcohol and were dried at 70°.

The specific rotation of this material in aqueous solution was +89.9°. After one recrystallization from hot aqueous alcohol and drying at 70° the crystals showed $[\alpha]_D^{20} = +88.2^\circ$. Their melting point was 148°. The acetyl derivative of the sugar,

¹ The identification by chemical means was confirmed by optical-crystallographic measurements made by Dr. Edgar T. Wherry, as described in the following article, p. 125.

prepared by the use of acetic anhydride and sodium acetate, crystallized readily from alcohol on the addition of water and showed the melting point 117° and $[\alpha]_D^{20} = +110.7^{\circ}$ in benzene and $+103.8^{\circ}$ in chloroform

These data agree completely with previously recorded measurements¹ by other observers and by ourselves on melezitose and its hendeca-acetate. The crystals of melezitose from the honey did not reduce Fehling's solution until after hydrolysis by acids, a property by which melezitose may be distinguished readily from the crystals of glucose that are commonly present in honey.

In the subsequent separation of larger quantities of melezitose from comb honey a more convenient method has been followed. Fifty g. of the comb honey was macerated in a mortar with 50 cc. of cold 80% alcohol, which thins out the sirupy portion but does not dissolve the crystals to any great extent, and the crystals and solid beeswax were filtered off through cloth and washed with cold 80% alcohol. The mixture of crystals and wax was then heated with a small quantity of water to dissolve the melezitose and melt the wax. After cooling, the upper layer of congealed wax was removed, and the solution was filtered with the aid of infusorial earth and evaporated to a sirup under reduced pressure. Some alcohol was mixed with the sirup and the melezitose rapidly crystallized. The crystals were washed with alcohol and dried at 70° . The yield from one section of the Port Royal comb honey was 20% melezitose, from another section 10%.

Comb Honey from Drummond, Montgomery County, Maryland.—Some two weeks after the isolation of melezitose from the Port Royal honey Dr. E. F. Phillips of the Bureau of Entomology, U. S. Department of Agriculture, who had become much interested in the subject, called our attention to the occurrence of a peculiar crystallization in honey combs that were being filled by bees at that time (July, 1918) in the vicinity of Drummond, Maryland. The crystallization formed in the comb with unusual rapidity, a phenomenon which had also arrested the attention of the producer of the Port Royal honey. Examination by the methods that have been described showed conclusively that the crystals in the Drummond honey were melezitose.

Comb Honey from Riverdale, Prince George's County, Maryland.—Dr. Phillips has also supplied a sample of crystallized comb honey from this locality, made during the 1917 season. It was found to contain about 16% of crystalline melezitose. Like the Port Royal honey it had also proved unwholesome winter food for bees.

The Source of the Melezitose in the Pennsylvania Honey.

In July, 1917, the bee-keepers at several places in central Pennsylvania noted that their honey was crystallizing shortly after the bees

¹ THIS JOURNAL, *Loc cit.*

placed it in the hives. Not only did this render the honey difficultly salable, but also when the honey was stored by the bees to be used as winter food, it proved to be unsuited to their requirements, and this, in connection with the unusual severity of the following winter, led to the loss from indigestion of many bee colonies. Coming as it did at a time of sugar shortage, when every effort was being made to increase the production of honey, this situation had a rather serious aspect; for it was not known but that it might be connected with some disease which would spread over a wide area, and lead to serious diminution in the honey supply. Mr. Charles N. Greene, Chief Apiary Adviser to the Pennsylvania Bureau of Economic Zoölogy—now the Bureau of Plant Industry—investigated the matter and obtained evidence that the honey in question was derived not from floral nectar but from honey-dew, the sweet fluid which collects on plants as the result of the activities of aphids and other insects. As far as could be determined at the time, the bees obtained this honey-dew from some species of pine tree, several of which are abundant in the region. Mr. Greene sent a sample of this honey to the Bureau of Entomology, U. S. Department of Agriculture, and that Bureau transmitted it to the Bureau of Chemistry with a request that its composition be studied. It was in this sample that the melezitose was first recognized.

At our request Dr. Edgar T. Wherry, Crystallographer of the Bureau of Chemistry, made a visit to Port Royal in June and August, 1918, and again in August, 1919, to obtain data on the origin of the melezitose in the Port Royal honey. On two of these trips he was accompanied by Mr. Greene, who aided in many ways the working out of the origin of the sugar. Information as to the occurrence of the material was obtained from H. L. Bowers of Port Royal and J. S. Colyer of Perulack, both in Juniata County; Prof. H. C. Klinger of Liverpool, Perry County; the Merrill Bee and Honey Co. of Muncy and C. V. Lorson of Williamsport, both in Lycoming County, Pennsylvania. Data as to the distribution of the various pines was obtained from Prof. J. S. Illick of the Pennsylvania Bureau of Silviculture; from the staff of the Pennsylvania Forest Academy at Mont Alto; and from Mr. Harold W. Pretz of Allentown. To all these gentlemen and others who coöperated in the investigation thanks are hereby extended. Dr. Wherry has submitted the following report of the results of his investigations:

"Five species of pine trees are common throughout the region studied: the white pine, *Pinus strobus* L., the table-mountain pine, *Pinus pungens* Michx. f., the yellow pine, *Pinus echinata* Mill., the pitch pine, *Pinus rigida* Mill., and the scrub pine (or jack pine as it is commonly called there), *Pinus virginiana* Mill. It was soon found that only the last of these was of significance in connection with the development of the melezitose. At a few localities, trees of this species, especially 4 or 5-year old

seedlings, were infested with a reddish brown soft-scale insect, which has been identified by the Bureau of Entomology as *Toumeyella parvicorne* Ckll.¹ As a matter of record the following specific places where it was observed in 1918 are listed: on hillside just back of Rockville, north of Harrisburg; on small ridge about 4 miles north of Liverpool; and in ravine about 2 miles south of Port Royal. At the Liverpool locality the honeydew produced by this insect was being actively collected by bees identifiable by their color and direction of flight to be those belonging to Prof. Klinger, whose place lies about half a mile away. Another point of interest about this locality was the fact that in one instance the same insect occurred on a young tree of *Pinus rigida*, which happened to be surrounded by numerous individuals of *P. virginiana*. It is also noteworthy that the water extract of honeydew-covered branches collected from these trees yielded on evaporation a quantity of nondescript gummy material, in which microscopic examination showed the presence of crystals, identifiable by their optical properties as melezitose. This indicates that the bees merely collect this sugar as it occurs, and do not synthesize it.

"Far more widespread than the above mentioned insect in all the localities in central Pennsylvania visited by the writer was a large gray to reddish aphid which has also been found at Drummond, Maryland, by Mr. Jacob Kotinsky of the Bureau of Entomology, U. S. Department of Agriculture; there are records on file of its occurrence also in Ohio, Virginia, and the District of Columbia. This insect was provisionally identified by Dr. A. C. Baker, of the Bureau of Entomology, as *Lachnus pineti* (Fab.) Koch. In the majority of the cases observed by the writer, and presumably in the others noted, the host plant was *Pinus virginiana*; occasionally a few insects were noted on *P. echinata* and *P. rigida*. This insect or a closely related species is said to be found in Europe more or less commonly, though never abundantly, on the Scotch pine, *Pinus sylvestris* L. This tree has been used in this country in considerable quantity for the purpose of reforesting some denuded hills, especially in central Pennsylvania, and the insects may have been introduced into this country on young trees of this species and spread from them to the native pine, *Pinus virginiana*, none could be found, however, on the numerous Scotch pine trees examined by the writer at several localities.

"In a grove of trees of *Pinus virginiana* in a ravine about 2 miles south of Port Royal, Pa., these insects were found to be common in 1918, and it was to the vicinity of this grove that Mr. Bowers, whose place is about a mile away, was able to trace his bees, which could easily be recognized by their color. What a large quantity of the melezitose must have been produced here is indicated by the results of the working up by the Bureau

¹ See Mr. Kotinsky's report on page 122.

of Chemistry of some honey obtained from Mr. Bowers. From 40 sections, which had been withdrawn from the hive before they were completely filled, we were able to extract over 5 kg. of the pure melezitose. Similar observations were made at every other place where melezitose formed; the producers had seen their bees working in or near colonies of this species of pine. One producer found his bees to collect honey-dew from a large tree of Norway maple, *Acer platanoides* L., at the time the melezitose appeared, but the relatively minute amounts of this sugar developed in his honey in 1918 may well have come from pines, which grow within a mile, and on which the aphid was found to occur.

"Only in exceptional seasons does melezitose-honey-dew appear to be collected by the bees. During the early part of July they obtain honey extensively from white clover, and about the first of August change over to buckwheat, which comes into bloom at that time. But if the weather is dry in mid-July the yield of white clover honey becomes scanty, and then the bees seek other sources of supply. The dry weather likewise permitting the accumulation of the honey-dew on the pine trees, they soon discover that this material is sweet, and collect it in large quantities. In both 1917 and 1918 there were long dry spells at the critical period, and large amounts of melezitose appeared in the honey. In 1919, however, the weather was wet during the greater part of July, and, although aphids and scales flourished, no melezitose whatever appears to have been collected, the clover honey lasting over until the buckwheat began to yield, and the rain keeping the honey dew from collecting on the pine branches.

"In order to complete the identification of *Pinus virginiana* as the source of the melezitose it seemed worth while to ascertain whether the development of this sugar in honey is, in fact, limited to the region in which this tree occurs. This pine may be classed as a southern species, as its range is rather sharply limited on the north at about latitude $41^{\circ} 30'$. It occurs rarely on Long and Staten Islands, New York, thence it appears sporadically in the Highlands of northern New Jersey. It is present in the Wyoming Valley up to a short distance north of Wilkes-Barre, Pa.; further west it has been found to reach a northern limit in the hills several miles north of Williamsport, in the Susquehanna valley. From here the northern boundary of its range swings southwestward to Pittsburgh, Pa., and it enters the southeastern part of Ohio, being included in lists of the plants of that state. As far as known it is bounded on the west by a line running thence southward to the Gulf states; and between this line and the coast it occurs at many places. It appears to be limited, however, to soils considered by the agriculturist as sterile and barren, the reaction of which is decidedly acid; thus it occupies old, "worn-out" fields throughout its range; it occurs on dry shale and sandstone soils throughout the Appala-

chian mountains, and on the sands of the Coastal Plain. In no case has melezitose been found in any honey produced outside of the area described, at least east of the Rocky Mountains, reports of crystallization in honey further north and west having proved on examination to be due to glucose and not to melezitose. The tracing of the source of the melezitose in the honey to this species of pine, therefore, seems justified."

Mr. Jacob Kotinsky, Entomological Assistant in the Bureau of Entomology, U. S. Department of Agriculture, has transmitted the following report on the identity of the scale insect found on the scrub pines, on the way such insects produce honey-dew, and on the possibility of preventing the development of melezitose:

"The insect on the pine twigs that were collected near Liverpool, Pa., by Dr. Wherry late in June, 1918, was identified by Mr. H. Morrison, a Bureau specialist on the classification of the group, as *Toumeyella parvicorne* (?) Ckll (Order, Homoptera: Family Coccidae). The insects were immature, which accounts for his query on the specific identity. *T. parvicorne* is one of the group of scale insects known as 'soft' or 'brown' scales, and is confined to pine trees. True to its affiliations, it feeds on sap, which it procures by means of a slender proboscis forced into the plant tissue and used as a conveyance of the substance pumped by muscles located at the proximal end of the organ. The developmental stage of the insect on the date that the specimens were brought to this office (July 2) indicates that *T. parvicorne* produces but one generation annually in the latitude and altitude of Liverpool and hibernates in the larval form, though these facts still remain to be determined definitely by observation. The family of scale insects (Coccidae) is closely allied to the Aphidae, the most common and best known honey dew producing insects, and, like them, various 'brown' or 'soft' scales and mealy bugs, when in large colonies, are sometimes capable of producing prodigious quantities of honey-dew. In the 'brown' or 'soft' scales, to which *Toumeyella parvicorne* belongs, production of honey-dew is the work of females only, is heaviest in the pre adult stage and is doubtless further conditioned by the part of the plant inhabited and by meteorological conditions. A young, growing shoot, itself favored by liberal precipitation, yields its sap more readily in such weather. Normally, honey-dew is washed off by rains and, therefore, accumulates more readily in dry weather. The presence or absence of ants, which usually accompany honey-dew producing insects, and other honey-dew gathering insects, especially aculeate (stinging) Hymenoptera, as well as the growth of the sooty fungus (*Meliola* sp.) obviously gage the quantity of honey-dew available for hive bees. A suggestive peculiarity of many species of these insects is that their feeding tends to produce deformities in the host tissues which, in some cases, become galls.¹

"Three methods of preventing the development of melezitose suggest themselves, i. e., to kill the honey-dew producing insects by encouraging their natural enemies, by spraying the infested trees with an insecticide, or by cutting out the trees subject to infestation. But, when it is realized that normally bees range two miles or more, the impracticability of the last two suggestions is obvious. The first one may likewise be dismissed for the reason that there is no way known to encourage the natural enemies of the insects in question.

"Dr. E. F. Phillips suggests that the control of this condition resolves itself, therefore, into disposing of the product as 'honey-dew honey' and providing for winter

¹ A. C. Baker, U. S. Dept. Agr., Rept. 101, 34 (1915), records finding unusually high sugar and low starch content in galls produced by the woolly apple aphid.

stores of each colony a supply of digestible sugar, so placed that this material will be first used during wintering. This is readily done, for example, by feeding sugar sirup or good honey to each colony after brood rearing has ceased. If it is stored below all other stores it will be first used."

Analytical Data on Honey Containing Melezitose.

It may be useful in connection with the general subject of the chemical analysis of honey to record the analytical data on the Port Royal honey. Two sections of it were examined, denoted as Samples 1 and 2. Sample 1 contained only a small quantity of crystalline melezitose but Sample 2 had crystallized solidly. The comb honey was dissolved in water, the insoluble wax, etc., filtered off, and the filtrate evaporated under reduced pressure to the consistency of honey. Polarizations and estimations of reducing sugars both before and after the Clerget (cold) inversion, using both hydrochloric acid and invertase as hydrolysts, were made on the liquid honey. All polarizations are calculated to the basis of 26 g. of liquid honey in 100 cc. of solution, read in a 200 mm. tube in a saccharimeter with the Ventzke scale. The percentage of solids in the liquid honey was determined by the refractometer, Sample 1 showing 75.5% and Sample 2, 77.1%. The reducing sugars are calculated as invert sugar. The measurements on the inverted solutions were made after 24 hours standing and also after 5 days and agreement was obtained for the two sets, proving that the hydrolyses were complete in 24 hours.

ANALYSIS OF THE PORT ROYAL, PENNSYLVANIA, HONEY OF HONEY-DEW TYPE

Sam- ple No	Polarisation						Reducing sugars					
	Direct		HCl inversion		Invertase inv		Sucrose invertase Clerget %		Direct		Invert	
	21°	87°	21°	87°	21°	87°	%		%	HCl	Inver- tase	Sucrose by Inver- tase
1	9.5	+12.6	-12.50	+11.00	11.75	+11.20	1.71	67.58	69.35	68.96	1.31	
2	27.9	+43.8	+17.60	+35.64	27.05	+44.00	0.65	42.00	63.08	42.73	0.69	

What is probably a close approximation to the percentage of melezitose present in the samples may be calculated in the following manner from the data of the table. In Sample 2 the percentage of sucrose that is shown by the Clerget method, using invertase as the hydrolyst, is 0.65%, and by the increase in reducing sugars after inversion with invertase 0.69%. These values agree well and it is probable that the action of invertase, which hydrolyzes sucrose but not melezitose, furnishes the most reliable estimation of sucrose in such products.¹ Using the average, 0.67%, the weight of sucrose in the normal weight of honey, 26 g., is $(26)(0.0067) = 0.17$ g. The change of rotation that is caused by the inversion of 26 g. of sucrose, readings being made at 21°, is known to be $142.7 - (21 + 2) = 132.5^\circ$, hence the change due to 0.17 g. is 0.86° . Now the acid inversion of the honey causes a change in rotation towards the negative side of 10.3° and if the change that is known to be due to the sucrose, 0.86° , be

¹ Hudson, *J. Ind. Eng. Chem.*, 2, 143-6 (1910).

subtracted, the difference, 9.4° , may be used as a basis for estimating the amount of melezitose that is present. Since¹ 26 g. of melezitose in 100 cc. of solution rotates $+134^\circ$ V. before hydrolysis and $+95.5$ afterwards, the quantity of melezitose present in 26 g. of the honey is calculated to be $(9.4)(26) \div (134 - 95.5) = 6.3$ g., and the percentage of melezitose is $6.3 \div 26 = 24.2\%$. A similar calculation can be based upon the increase in reducing sugars after the hydrolysis of the honey by invertase and by acid. The increase through the action of invertase is $42.73 - 42.00 = 0.73\%$ invert sugar, while the acid hydrolysis shows an increase of $63.08 - 42.00 = 21.08\%$, calculated as invert sugar. Attributing the difference, $21.08 - 0.73 = 20.35$, to the hydrolysis of melezitose, it is noted first that this much invert sugar is equivalent in reducing power to 20.35 (0.95) = 19.3% of *d*-glucose, and second that 100 g. of melezitose is known¹ to have the same reducing power after hydrolysis as 69 g. of *d*-glucose. Hence the percentage of melezitose present in the honey is $19.3 \div 0.69 = 27.9\%$. Similar calculations indicate that Sample 1 contained 1.96% melezitose, according to the polarization data, and 0.54% according to the reducing sugar estimations. While these methods of analysis leave much to be desired in the way of accuracy, they are nevertheless fairly satisfactory approximations in a case where all methods of analysis that have been employed in the past in the examination of honey fail completely. In the future when a honey is found by the analyst to show a large increase in reducing sugars by acid inversion, but a much smaller increase by invertase hydrolysis, the presence of melezitose should be suspected. On the other hand, no honey should be condemned as being adulterated with sucrose on the sole basis of an increase in reducing sugars by acid hydrolysis because the presence of melezitose can equally well cause such an increase. The quantity of sucrose in a honey should be estimated by inversion with invertase.

Honey which contains so much melezitose as does Sample 2, over 20%, will deposit crystals of this sugar readily, but if the honey is in liquid form, through heating, for example, the melezitose may best be crystallized by fermenting away the other sugar with baker's yeast. Forty g. of Sample 2 was diluted with water to a solution of about 20% solids and fermented several days with baker's yeast. When no further gas bubbles were observed the solution was clarified by filtration through a little infusorial earth and evaporated to a thick sirup, which soon crystallized and yielded 8.3 g. of melezitose or 20.7% of the weight of the honey, a very good yield. Possibly this method of crystallizing melezitose from honey may prove useful in detecting the sugar in cases where its presence in honey is suspected from analytical data.

¹ THIS JOURNAL, 40, 1456-60 (1918).

Summary.

It has been known since ancient times that bees collect mannas during droughts because floral nectar is not then abundant. Turkestan manna and likewise a manna from the European larch tree have long been known to contain the rare sugar melezitose, and recently we have found over 70% melezitose in a manna from the Douglas fir of British Columbia. Might not melezitose be present, therefore, in some kinds of honey and have escaped detection in the past? While considering this question we received a sample of comb honey, of honey dew type, from Port Royal, Pennsylvania, which had crystallized solidly in nearly all the cells. The crystals were not *d*-glucose, the sugar that frequently crystallizes from honey, but were pure melezitose. Two samples of honey-dew honey from Maryland have also been found to contain crystals of melezitose. An investigation by Dr. Edgar T. Wherry of the origin of these 3 lots of honey discloses that the bees collect a sweet fluid deposited on the young twigs of the Virginia pine (*Pinus virginiana*) by a soft scale insect (*Toumeyella parvicorne* (?) Ckll), or at other times by an aphid (*Lachnus pineti* (Fab.) Koch), and store away this material in place of floral nectar. The fluid itself was found to contain melezitose. Analytical data on this type of honey are recorded, and a way for the approximate estimation of melezitose in such products is described. Since melezitose has already been identified in mannas from two conifers, namely the European larch and the Douglas fir, and is now found in an exudation from a third, the scrub pine, the question naturally arises, whether melezitose may not be present in the sap of most coniferous trees. In making this query it is assumed that the insects that produce these mannas and exudations do not synthesize the melezitose; this assumption seems quite probable, though it remains to be established.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE CRYSTALLOGRAPHY OF MELEZITOSE.

By EDGAR T. WHERRY

Received September 16, 1919

Crystallography.

The existing data as to the crystallography of the trisaccharide melezitose is not only incomplete but contradictory. Villiers¹ described it as monoclinic, bounded by a prism, *m*, the base *p*, and the side pinacoid *g*₁; he obtained the angles *g*₁ : *m* = 136° 38' and *m* : *p* = 92° 40'. On the other hand Alekhine² found it to be rhombic, his crystals showing

¹ *Compt. rend.*, 84, 37 (1877); *Bull. soc. chim.*, 27, 100 (1877).

² *J. Russ. Soc. Phys. Chem.*, 21, 411 (1889); *Ann. chim. phys.*, [6] 18, 338-9 (1889).

front and side pinacoids, o and a , prism, m , and front and side domes, od and ga , although he recorded no measurements at all. In both cases the dihydrate is supposed to have been represented, but no information has been available to indicate whether this was a case of dimorphism or whether the two authors were in fact not dealing with the same substance.

The recent discovery by Hudson and Sherwood¹ of this sugar in relatively large quantities from two widely separated regions in the United States¹ has given an opportunity to study the matter further.

A sample of material from Pennsylvania was dissolved in an excess of water and filtered into a small beaker, which was covered with filter paper and allowed to stand at ordinary temperature for several days. The crystals which separated attained a diameter of a millimeter, but were crowded together to such an extent as to make them unsuitable for crystallographic measurements. A few minute simple ones were picked out, and the balance redissolved by addition of a little water and warming. The liquid was then allowed to cool and the crystals previously picked out were introduced, the vessel being allowed to stand in a room kept at a constant temperature of 20° for several days. The same procedure was followed, using 50% alcohol as the solvent.

The crystals which separated proved to be rhombic, those from water being broader than those from alcohol, and both types showed the same forms as those described by Alekhine. In the following description his orientation is retained, although the lettering of the forms is changed so as to bring it into accord with modern practice. The faces are somewhat rounded as well as distorted by subparallel intergrowth, so that the measurements vary as much as $\pm 30'$, but the general features of the crystallography can be readily established. The average angular values and the derived axial ratio are presented in Table I.

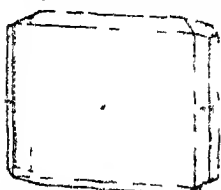


Fig. 1.—Melezitose crystal

TABLE I
Angle-Table for Melezitose Dihydrate, $C_{12}H_{22}O_{11} \cdot 2H_2O$
System, rhombic, seemingly holohedral, but no doubt bisphenoidal
Axes $a \ b \ c = 1 \ 216 \ 1 \ 0 \ 496$

No.	Form.	Symbol		Description	Observed		Calculated	
		Gdt.	Mill.		$^{\circ}$, $'$	$^{\circ}$, $'$	$^{\circ}$, $'$	$^{\circ}$, $'$
1	b	00	010	Narrow, somewhat dull	0 00	90 00	0 00	90 00
2	a	00	100	Prominent, brilliant	90 00	90 00	90 00	90 00
3	m	00	110	Narrow, but good	38 03	90 00		90 00
4	e	01	011	Small, somewhat rounded	0 00	26 30	0 00	26 24
5	d	10	101	Prominent, brilliant	90 00	21 15	90 00

Many crystals showed only the forms b , a , and d ; and it is possible that Villiers' measurements were made on greatly distorted crystals of this

¹ THIS JOURNAL, 40, 1436-60 (1918). See also the preceding article.

development, b being his p , a his g_1 , and d his m . The complete set of forms observed is shown in Fig. 1.

Optical Properties.

Under the microscope melezitose presents the form of plates and rods, in part rectangular in outline and in part terminated by faces inclined at large angles (see Fig. 2). On crushing the crystals, irregular flakes are produced.

The rectangular plates yield on immersion in oily liquids of known refractive index the values of β and γ , but crushed fragments usually show values intermediate between α and β in one direction. Observations were made in light of variable wave length, obtained by a monochromatic illuminator, at 20° . The dispersion relations were found to be as stated in Table II.

TABLE II
Refractive Indices of Melezitose for Different Wave Lengths.

Index	Wave length					
	450	500	550	D, 589	600	650.
α	1.550	1.546	1.542	1.540	1.540—	1.538
β	1.558	1.553	1.550	1.548	1.547	1.545
γ	1.561	1.556	1.552	1.550	1.549	1.547
$\gamma - \alpha$	0.011	0.010	0.010	0.010	0.009+	0.009

The refractive indices for sodium light are thus $\alpha = 1.540$, $\beta = 1.548$, and $\gamma = 1.550$, all ± 0.001 . The total double refraction is 0.010 but that usually seen is the difference between γ and β , or 0.002.

In parallel polarized light the double refraction of the plates is seen to be weak, and the colors are mostly brilliant grays of the first order. Rod-like fragments may show white or yellowish colors, corresponding to the maximum double refraction. The extinction is straight and the sign of elongation usually +.

In convergent polarized light, on thick plates, a good biaxial interference figure is obtained, the axial angle $2E_D$ being large, 85° , and the character, —. The orientation is $X = a$, $Y = b$ and $Z = c$.

Certain of these properties, especially the habit and the weak, double refraction, may be turned to account in the identification of this sugar in honeys or honey-dews. The d -glucose which frequently crystallizes out in honeys is in rods terminated at one end by planes lying 60° apart and rounded at the other end (Fig. 3); and in parallel polarized light showing at least in the centers of the grains brilliant colors of the second



Fig. 2 — Melezitose under the microscope



Fig. 3 — Glucose under the microscope.

order, with — elongation. If the sirupy honey is removed from around these crystals by glacial acetic acid and the refractive indices are determined by the immersion method, the α of *d*-glucose is found to be about one unit in the second decimal place lower than that of melezitose, and the γ a like amount higher. Sucrose can also be readily distinguished from melezitose by its much greater double refraction, α being 1.45 and γ 1.57, and by breaking into irregular fragments with oblique extinction.

It is believed that this method of examination of the crystals which develop in honeys will be of much aid in the systematic search for the occurrence of melezitose.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE PREPARATION OF PARA-UREIDO-PHENYLACETYLUREA, AND RELATED COMPOUNDS.

BY MARY RISING¹

Received October 20 1919

A study of the preparation of ureido phenylacetylurea was begun by the author, with the aid and advice of Professor Stieglitz, following the publication some time ago of the work upon the synthesis of phenylethyl-barbituric acid². Phenylethyl-barbituric acid (luminal), widely used in the treatment of epilepsy, has hypnotic and sedative properties. Under certain conditions, the drug is known to have a toxic effect, and for this reason its use cannot be prescribed in all cases. With time of peace at hand, when there is leisure to work along lines of theory, rather along those laid down by the imperative demands of war needs, the building up of a new series of compounds, related chemically to phenylethyl-barbituric acid, was undertaken. The effort has been made to retain in these compounds the excellent hypnotic properties of phenylethyl-barbituric acid, avoiding meanwhile those properties which are harmful. The compounds prepared in this way are to be thoroughly tested physiologically, in the hope of discovering a hypnotic of even greater value than is phenylethyl-barbituric acid.

The fact that phenylethyl barbituric acid possesses toxic properties which are not possessed by the closely related compound, diethyl-barbituric acid, suggested the toxicity of the phenyl group. For the modification of the phenyl group, we have first tried the introduction in the phenyl radical of a urea group, which might at the same time enhance the hyp-

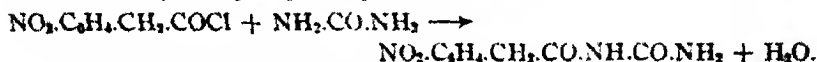
¹ The material given in this report will be included in the dissertation of the author in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Chicago

² Rising and Stieglitz, *THIS JOURNAL*, 40, 4, 725 (1918).

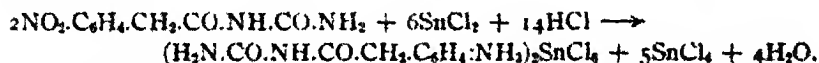
notic properties. Further, in place of the use of a dicarboxylic acid radical as in diethyl-barbituric acid (veronal), and in phenylethyl-barbituric acid, a monocarboxylic acid, phenylacetic acid, was first used, as in the case of the hypnotic diethylbromo-acetylurea (adalin), as giving products easier of approach. Finally, we are introducing into our compounds ethyl groups, and bromine, which have, as is well known, hypnotic properties. These considerations have led us to undertake the preparation of the following group of compounds: (1) *p*-Ureido-phenyl-acetylurea. (2) *p*-Ureido-phenylethyl-acetylurea. (3) *p*-Ureido-phenyldiethyl-acetylurea. (4) *p*-Ureido-phenylethyl-bromoacetylurea. The preparation of the first of these compounds is described in this paper.

p-Ureido-phenyl-acetylurea was made on the basis of the following series of reactions:

(1) *p*-Nitrophenyl-acetyl chloride is condensed with urea in boiling benzene, and *p*-nitrophenyl-acetylurea is formed.¹



(2) *p*-Nitrophenyl-acetylurea is reduced quantitatively to *p*-aminophenyl-acetylurea by means of stannous chloride in glacial acetic acid in the cold.²

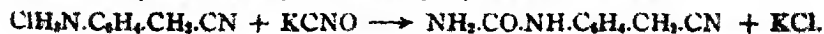


(3) The hydrochloride of *p*-aminophenyl-acetylurea is treated with potassium cyanate, whereupon rearrangement takes place, and *p*-ureido-phenyl-acetylurea is formed.

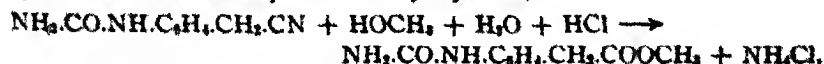


Some preliminary preparations of related urea derivatives are first to be described:

(1) The hydrochloride of *p*-aminobenzyl cyanide was treated with potassium cyanate, and *p*-ureidobenzyl cyanide was formed.



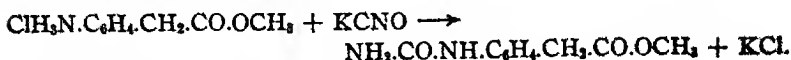
(2) The methyl ester of *p*-ureido-phenylacetic acid is prepared: (a) by the esterification of *p*-ureidobenzyl cyanide,



¹ Jacobs and Heidelberg, THIS JOURNAL, 39, 2418 (1917).

² Weyl, *Die Methoden der organischen Chemie*, 2, 211 (1909); cf. Thiele and Dimroth, *Ann.*, 305, 114 (1899). The first product isolated (see below), is the chlorostannate. Jacobs and Heidelberg (*Loc cit.*), effected this reduction with ferrous sulfate and ammonia.

and, (b) by the action of the hydrochloride of *p*-amino-phenylacetic methyl ester with potassium cyanate.



(3) By the hydrolysis of *p*-ureido-phenylacetic methyl ester, *p*-ureido-phenylacetic acid is obtained.

The ethylation of benzyl cyanide, preliminary to the preparation of *p*-ureido-phenylethyl-acetylurca and the other compounds listed above, will be discussed below in connection with the preparative details.

Experimental Part.

Benzyl cyanide was converted into *p*-nitrobenzyl cyanide according to the method of Pschorr, Wolfes, and Buckow.¹ The method of these authors, together with certain modifications suggested by Hanke,² was used for the reduction of nitrobenzyl cyanide. *p*-Aminobenzyl cyanide, prepared in this way, was used in the synthesis of the first of our ureids.

1. *p*-Amino-phenylacetic Methyl Ester, *p*-NH₂.C₆H₄.CH₂.CO.OCH₃.—The hydrochloride of the ester is prepared according to the method used by us for the preparation of phenylacetic methyl ester in the synthesis of phenylethyl-barbituric acid.³ To a mixture of absolute methyl alcohol (112 g.), and water (6 g.) is added *p*-aminobenzyl cyanide (28 g.). When the saturation with hydrogen chloride is begun, the hydrochloride of *p*-aminobenzyl cyanide is precipitated. As the reaction progresses, the hydrochloride goes into solution gradually, and after some time a precipitate of ammonium chloride appears. When the process of esterification is complete, the alcoholic solution is cooled, decanted from the ammonium chloride, and almost all the alcohol evaporated *in vacuo*. On cooling, a heavy mass of the hydrochloride of *p*-amino-phenylacetic methyl ester settles out and is collected on a filter. The crude yield from 28 g. of cyanide was 32 g., containing some ammonium chloride. It was purified in the following way: A mixture of one part of absolute alcohol and 4 parts of dry ether was prepared, and 60 cc. of this solution shaken with 3 g. of the impure hydrochloride in a separatory funnel. All but a small sediment of ammonium chloride dissolved, and the supernatant solution of the hydrochloride was siphoned off. This solution was evaporated to 1/2 its volume *in vacuo*, the residue cooled, and a heavy mass of nearly white, silvery leaves obtained, which is the hydrochloride of *p*-amino-phenylacetic methyl ester. An analysis for chlorine showed the

¹ Ber., 33, 17 (1900).

² Dr. Milton Hanke's paper including this preparation is shortly to appear in THIS JOURNAL.

³ Loc. cit.

product to be pure. The analysis of the hydrochloride of this same ester as prepared by Salkowski¹ showed a very high chlorine content.

Subs., 0.1095: 0.1 *N* AgNO₃, factor 0.967, 5.59 cc.

Calc. for C₈H₁₂O₂NCl: Cl, 17.60. Found: 17.50.

The hydrochloride was dissolved in 25 cc. of water and the solution made just alkaline with sodium hydrogen carbonate, methyl orange being used as indicator. The solution was then titrated with silver nitrate in the usual way, potassium chromate being used as indicator.

The free base was prepared from the hydrochloride as follows: The hydrochloride (4 g.) was dissolved in 20 cc. of water and 50 cc. of ether was added. The calculated amount of sodium hydrogen carbonate (2.1 g., dissolved in 30 cc. of water) was added in small portions, and the whole shaken in a separatory funnel. The ether layer was separated, and the aqueous residue extracted twice with ether. The ether extractions were combined and dried over sodium sulfate, the ether evaporated, and the remaining oil fractionated. At 75°, and 20 mm. pressure, the oil commenced to boil. At 140–150° and 17 mm. pressure the main fraction, the ester itself, distilled. At 155° and 17 mm. pressure a last fraction was obtained. Salkowski gives no boiling point in his description of the amino ester.

2. *p*-Ureidobenzyl Cyanide, *p*-NH₂.CO.NH.C₆H₄.CH₂CN.—The hydrochloride of *p*-aminobenzyl cyanide is prepared by precipitation with dry hydrogen chloride from the solution of the free base in dry ether. The hydrochloride (13 g.), obtained in this way, is dissolved in 75 cc. of water, and to this solution is added potassium cyanate (7 g., the calculated amount and 1/3 excess, dissolved in 24 cc. of water). There is slight effervescence, due to the formation of cyanic acid, and the solution thickens to a pasty mass as the ureido compound forms. This mixture is evaporated to dryness on the water bath, extracted with water to remove potassium chloride formed in the reaction, and any unchanged potassium cyanate, and the undissolved residue is collected on a filter. Recrystallization of this residue from 95% alcohol yielded a product melting sharply at 170.5°.

Subs., 0.0514: 10.92 cc. N (over 50% KOH) at 22° and 752.5 mm. (24°).

Calc. for C₈H₇N₃O: N, 24.00. Found: 23.91.

3. *p*-Ureido-phenylacetic Methyl Ester, *p*-NH₂.CO.NH.C₆H₄.CH₂.CO.OCH₃.—This compound was prepared in two ways: (a) by the esterification of *p*-ureidobenzyl cyanide, and (b) from *p*-amino-phenylacetic methyl ester hydrochloride by treatment with potassium cyanate.

(a) *Esterification of p*-Ureidobenzyl Cyanide.—The ureidobenzyl cyanide (7 g.) is dissolved in a mixture of absolute methyl alcohol (42 g.) and water (2 g.). The process of esterification used in the preparation of

¹ Ber., 28, 1919 (1893).

p-amino-phenylacetic methyl ester is carried out. When the alcoholic solution is decanted from the ammonium chloride formed in the reaction, it is set aside for a few hours, and presently a precipitate of white crystals of the ureido ester separates. The crystals are collected on a filter and are found to melt at 110° . The yield of crude material was 4.5 g. Recrystallization from 95% alcohol gave a product melting at 132° .

(b) *Action of Potassium Cyanate on p-Amino-phenylacetic Methyl Ester Hydrochloride*.—The hydrochloride (6 g.) is dissolved in water (48 cc.) and potassium cyanate (4.2 g., the calculated amount and $\frac{1}{2}$ excess, dissolved in 10 cc. of water) is added. The reaction seemed to go to completion at once, and the pasty product of the reaction was not evaporated to dryness as in other similar preparations. When evaporation was carried out over the water bath, ammonia fumes were given off, showing decomposition. The mass was allowed to stand in the cold for about an hour, and was then collected on a filter and washed thoroughly with water. A yield of 5.6 g. of crude ester was obtained. It was recrystallized by solution in the smallest possible amount of warm 95% alcohol, and precipitation from this solution with a large volume of ether. White, shining needles were obtained in this way, of melting point $131-132^{\circ}$.

Subs., 0.1259 18.22 cc. N (over 50% KOH), at 19° and 749.2 mm

Calc. for $C_{10}H_{12}N_4O_3$ N, 13.46 Found 13.46

4. *p*-Ureido-phenylacetic Acid, $p-NH_2.CO.NH.C_6H_4.CH_2.COOH$.—This acid was first prepared by Traube.¹ Our preparation by the hydrolysis of *p*-ureido-phenylacetic methyl ester and recrystallization from alcohol gave a purer product. It melted with decomposition at $184-185^{\circ}$. (Traube, m. p. 174° .)

Subs., 0.1285 17.00 cc. N (over 50% KOH) at 28° and 747.3 mm (28°).

Calc. for $C_9H_{10}N_4O_4$ N, 14.43 Found 14.32

The Preparation of *p*-Ureido-phenyl-acetylurea.

1. *p*-Nitro-phenylacetic Acid, $p-NO_2.C_6H_4.CH_2.COOH$.—The acid was prepared according to the method of Gabriel.² A quantitative yield was obtained, m. p. 151° . (Gabriel, m. p. $151.5-152^{\circ}$.)

2. *p*-Nitro-phenylacetyl Chloride, $p-NO_2.C_6H_4.CH_2.COCl$.—*p*-Nitro-phenylacetic acid, prepared as indicated above, was converted into its chloride by the method described by Wedekind.⁴ A quantitative yield of *p*-nitro-phenylacetyl chloride was obtained, m. p. $42-45^{\circ}$, which was considered sufficiently pure for use. (Wedekind, m. p. 47° .)

3. *p*-Nitro-phenyl-acetylurea, $p-NO_2.C_6H_4.CH_2.CO.NH.CO.NH_2$.—*p*-Nitro-phenylacetyl chloride was converted into *p*-nitro-phenyl-acetyl-

¹ Ber., 15, 2121 (1882)

² Traube found 14.04% N.

³ Ber., 15, 834 (1882).

⁴ Ann., 378, 289 (1911).

urea by treatment with urea in benzene solution.¹ When the reaction was complete the *p*-nitro-phenyl-acetylurea was collected on a filter. The crude material turned brown at 220° and melted with decomposition at 230°. Its purification was accomplished by recrystallization from warm, glacial acetic acid, or from amyl alcohol. The purified product turned slightly yellow at 230°, softened somewhat at 233°, and melted to a reddish brown liquid at 237–239°.² This liquid solidified on cooling, and when put in the bath again at 225°, melted.

Subs., 0.1027 17.73 cc. N (over 50% KOH) at 26° and 746 mm (23°)

Calc. for C₈H₈O₂N₂: N, 18.83 Found 18.84

4. *p*-Amino-phenyl-acetylurea, *p*-NH₂.C₆H₄.CH₂.CO.NH.CO.NH₂.—The reduction of *p*-nitro-phenyl-acetylurea was accomplished with stannous chloride in glacial acetic acid which was saturated with hydrogen chloride. The following method was found to be very successful, with each step in the process well defined: Its main advantage lies in the fact that the reduction takes place in the cold. The urea derivative had shown itself to be rather unstable when kept at a high temperature for any length of time. Dry hydrogen chloride was passed into 60 cc. of glacial acetic acid to saturation. To this acid was added 3 mols. of crystallized stannous chloride and 50% excess, in all, 11.6 g. of 85% stannous chloride being used. The acid was heated slightly to dissolve the stannous chloride. The mixture was then cooled and *p*-nitro-phenyl-acetylurea (2 g.) added, and a stream of dry hydrogen chloride led into the flask, while the contents of the flask were stirred gently with the aid of a motor. After about 10 minutes, the urea was dissolved completely. Within 15 minutes more a heavy, white precipitate settled out of the solution, which proved to be the complex tin salt of the amine. The flask meanwhile became somewhat warm from the heat of reaction. The stirring was continued till the mixture was quite cool (for about one hour). At the end of that time the tin salt was collected. When dry, the yield of this salt was 4.1 g., the mass probably containing some stannous chloride, and the crystals being somewhat solvated.

The free base was obtained as follows: The tin salt was dissolved in water and the solution made sufficiently acid with hydrochloric acid to give a blue-green tint with methyl violet.³ Tin sulfide was then precipitated with hydrogen sulfide, about an hour and a half being used for a complete precipitation. The stannic sulfide was removed by filtration and the filtrate concentrated *in vacuo* at 45° to a small volume. It

¹ Later we found that Jacobs and Heidelberger (*Loc. cit.*) had prepared this compound by practically the same method.

² As decomposition occurs at this temperature, the melting point depends largely on the speed with which the bath is heated. Jacobs and Heidelberger give the melting point as 250–2°, with complete decomposition.

³ Stieglitz, *Qualitative Analysis*, 1, 214 (1913).

was then made slightly basic with ammonia when a heavy precipitate of slender, white needles settled out. The base thus formed may be recrystallized by solution in acid and reprecipitation with ammonia, or it may be recrystallized from boiling water, in which it is fairly soluble. It does not melt, but decomposes at $192-3^{\circ}$. The yield of the pure compound was 1.2 g., or 70% of the theoretical amount.¹

Subs., 0.0551: 10.75 cc. N (over 50% KOH) at 21.5° and 748.5 mm. (24°).

Calc. for $C_9H_{11}O_2N_3$: N, 21.76 Found. 21.83

5. *p*-Ureido-phenyl-acetylurea, $p-NH_2.CO.NH.C_6H_4.CH_3.CO.NH.CO.NH_2$.—The hydrochloride of *p*-amino-phenyl-acetylurea was prepared by solution of the base (0.5 g.) in *N* hydrochloric acid (2.57 cc.). To this solution of the hydrochloride was added a solution of 0.28 g. of potassium cyanate (1 mol. and $\frac{1}{2}$ excess) in 10 cc. of water. After the addition of the cyanate, the mixture became at once thick and pasty, and was evaporated to dryness on the water bath. The residue was then taken up in a little water to remove the potassium chloride formed in the reaction and the solid collected on a filter. The ureido-ureid was found to be quite soluble in hot water and is recrystallized from it. The yield of purified product was 0.47 g., or 77.5% of the theoretical amount.

Subs., 0.0816 17.40 cc N (over 50% KOH) at 21° and 745 mm (22°)

Calc. for $C_{10}H_{12}O_4N_4$: N, 23.72 Found: 23.79.

The Ethylation of Benzyl Cyanide.

α -Phenylbutyronitril, $CH_3.CH_2.CH(C_6H_5).CN$.—The substitution of an alkyl group for one of the aliphatic hydrogens in the benzyl cyanide molecule takes place in two stages, the formation of a sodium salt and the replacement of sodium by the ethyl group.²

The completeness of the reaction in which α -phenylbutyronitril is formed depends, first of all, clearly upon the formation of a maximum amount of the sodium salt of benzyl cyanide. In the first attempt to prepare this sodium salt, metallic sodium was used, but the method of Bodroux² for the preparation of α -phenylbutyronitril was otherwise followed. Bodroux used sodium amide in place of metallic sodium.

Fine sodium wire (2.4 g.) is placed in 40 cc. of sodium-dried ether, under a reflux condenser. Benzyl cyanide (12 g.) is then dropped slowly into the flask containing the sodium and ether, two or three drops of absolute alcohol are added, and the reaction begins promptly. The ether boils, and most but not all of the sodium dissolves in the course of an hour. At the end of that time the ether solution has turned red, and a mass of the sodium salt, mixed with small particles of sodium, is deposited on the bottom of the flask. The mixture is heated for half an hour over

¹ Jacobs and Heidelberger effected the reduction with ferrous sulfate. Their crude yield was 73% of the theoretical amount.

² *Bull. soc. chim.*, 4, Ser. 7, 666-667 (1910).

the water bath, and then cooled. Ethyl iodide (16 g.) is added slowly to the suspension of the sodium salt, whereupon the mixture becomes warm and boils, and a light colored precipitate (NaI) settles out. When the boiling has ceased, the contents of the flask are heated for half an hour over the water bath and are then treated with a little water to dissolve particles of sodium and the sodium iodide. The ether layer is separated and combined with ether extracts of the aqueous solution. The whole ether extract is dried with calcium chloride and the ether removed by evaporation. The residue from the ether solution is a dark red oil, which, when subjected to vacuum distillation, boils from 70-105°, at 10 mm. pressure, all but a few drops of the distillate passing over above 100°. The yield of distillate was 6.4 g.

When sodium amide¹ was used in the preparation of the sodium salt of benzyl cyanide, a better yield of the ethylated product was obtained. From 12 g. of benzyl cyanide, a yield of 10 g. of distillate boiling at 108-118°, at 12 mm., was obtained. This oil contains, as stated by Bodroux, α -phenylbutyronitril, and any unchanged benzyl cyanide. Since the boiling points of the two nitrils lie too close together to make a separation by fractionation possible, it was found necessary by us to saponify the nitrils, in order to effect a separation. Phenylacetic acid melts at 76°, and α -phenylbutyric acid at 42°. In order to determine the degree of completeness of the reaction just described, hydrolysis of the distillate of boiling point 108-118°, at 12 mm., was undertaken.

Our method of saponification was the following: The 10 g. of distillate was boiled for 8 hours with 15 g. of potassium hydroxide in 60 g. of 95% alcohol. At the end of this time the alcohol was distilled off *in vacuo* and the residue was extracted with ether to remove any unchanged nitrils. The alkaline solution was then made slightly acid with dil. hydrochloric acid and extracted with ether several times. The ether extracts were combined, dried over calcium chloride, and the ether evaporated. The residue, a thick oil, solidified slowly on standing *in vacuo*, and 10.3 g. of crystals were obtained melting at 37-40°. The crystals were mixed with some oily material, which was removed by purification. To this end, the oily crystals were dissolved in concentrated ammonia and the solution was cooled in a freezing mixture. To it was added slowly cold conc. hydrochloric acid and enough water to dissolve the ammonium chloride which formed. When an excess of acid had been added, the solution became turbid, and if it had been kept at a low temperature during the addition of the acid, the α -phenylbutyric acid precipitated out in fairly pure form. Crystals obtained in this way were slightly yellow and melted at 40-42°. From 12 g. of benzyl cyanide, a yield of 8.1 g. was obtained, or 48% of the theoretical amount.

¹ Bodroux, *Loc. cit.*

From a second preparation of α -phenylbutyronitril with sodium amide, in which 48 g. of benzyl cyanide was used, a yield of 49 g. of distillate boiling at $70-110^{\circ}$, at 10 mm, was obtained, all but a few drops of which distilled above 100° .

The distillate (6.4 g) from the ethylation of 12 g. of benzyl cyanide with metallic sodium was hydrolyzed and a yield of about 4 g. of α -phenylbutyric acid obtained, of melting point $41-42^{\circ}$.

An attempt to substitute calcium carbide for sodium amide and sodium in the action with benzyl cyanide was made, but proved unsuccessful, because the carbide was not attacked appreciably.

Summary.

The successful preparation of *p*-ureido-phenyl-acetylurea is described as the first of a series of ureidophenyl acyl derivatives of urea which are intended to form the basis for a study of their physiological activity, particularly as hypnotics. Intermediate products and their preparation are described. The preparation of other derivatives of the series, such as ureido-phenylethyl acetylurea and ureido-phenylethyl-barbituric acid, is well under way in this laboratory and will be reported on at a later date.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE]

METHYL AND ETHYL AMMONIUM MERCURIC IODIDES: THEIR PREPARATION, CRYSTALLOGRAPHY, AND OPTICAL PROPERTIES.

BY GEORGE S. JAMIESON AND EDGAR T. WHERRY

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The compounds described in this paper were obtained by adding potassium mercuric iodide (Mayer's reagent) to aqueous solutions of the amines which had been acidified with hydrochloric acid. Woodward and Alsberg¹ discovered that minute quantities of tertiary methyl and ethyl amines could be precipitated and detected by means of Mayer's reagent in the presence of the primary amines as well as the secondary amines provided the latter were present in small amounts. However, when one cc. of solution contains more than 20 mg. of diethylamine or more than 4 mg. of dimethyl amine, these compounds are precipitated with Mayer's reagent. In addition to the trimethyl and triethyl ammonium mercuric iodides described by Woodward and Alsberg, Woodward prepared tetramethyl ammonium mercuric iodide, which was recently found

¹ A paper on "A New Reagent for Volatile Tertiary Amines," was presented September, 1916, at the New York meeting of the American Chemical Society, and will be published later.

to melt at 236° , and the corresponding ethyl compound, which melts at 155° .

All of the substituted ammonium mercuric iodides were bright yellow in color and had the common property of being decomposed by water with the separation of red mercuric iodide. It was also observed that all of the compounds investigated were readily soluble in potassium iodide. It is of great importance, therefore, to prepare Mayer's reagent exactly as described below in order to avoid an excess of potassium iodide which would prevent the detection of small quantities of the tertiary amines as proposed by Woodward and Alsberg.

The methyl and ethyl ammonium mercuric iodides have been submitted to detailed crystallographic and optical investigation in order to obtain means for their identification.

Experimental Part.

Dimethyl Ammonium Mercuric Iodide, $(\text{CH}_3)_2\text{NH.HI.HgI}_2$.—This compound was prepared by adding a distinct excess of Mayer's reagent to a slightly acidified solution of dimethyl amine hydrochloride. The Mayer's reagent employed in this investigation was made of 45 g. of mercuric iodide and 33 g. of potassium iodide in water so as to make exactly 100 cc. of solution. It is important to weigh both of the iodides with care in order to avoid an excess of the potassium iodide in which all the substituted ammonium mercuric iodides are readily soluble. When Mayer's reagent was added to the dimethyl amine hydrochloride solution at room temperature, a heavy oil separated which was readily changed to a bright yellow crystalline meal by shaking the solution and cooling it to about 15° . The crystals were filtered with suction, washed twice with small portions of cold water, and thoroughly pressed on filter paper. Further washing must be avoided in order not to decompose the compound. The appearance of red mercuric iodide indicates decomposition. The filtrate was allowed to remain in an ice box for a day and a small crop of somewhat larger crystals was obtained. This compound was found to have an extraordinary solubility in alcohol and acetone. On the other hand it was almost completely insoluble in ether and chloroform. Many futile attempts were made to recrystallize this compound by dissolving it in alcohol or acetone together with various quantities of ether or chloroform. The compound was found to melt at 122° . An analysis for mercury gave the following result:

Subs., 0.3160; HgS , 0.1173.

Calc. for $(\text{CH}_3)_2\text{NH.HI.HgI}_2$: Hg , 32.02. Found: 32.08.

The analysis was made by dissolving the weighed portion in about 20 cc. of 20% sodium sulfide solution and the mercury sulfide was precipitated by adding a slight excess of 1 : 3 sulfuric acid. After heating for 5 minutes on the steam bath, the solution was allowed to stand until

the mercury sulfide had settled. The precipitate was collected in a Gooch crucible, washed with water, then with absolute alcohol, and the precipitated sulfur was extracted with carbon disulfide. The mercury sulfide was then dried at 100° and weighed.

A series of experiments was made in order to ascertain how small a quantity of dimethyl amine could be detected by Mayer's reagent, and it was found that no precipitate was obtained when less than 20 mg. of the amine per cc was present.

Trimethyl Ammonium Mercuric Iodide, $(\text{CH}_3)_3\text{N.HI.HgI}_2$.—This compound, which was first prepared by Woodward and Alsberg, was obtained in the same manner as the previous one described above, except that it is not necessary to cool the solution because it separates at once in a crystalline form. After filtering the crystalline precipitate and pressing it on filter paper, it was dissolved in warm 95% alcohol and as the solution gradually cooled, long, slender, yellow prisms separated. It is very easy to grow crystals 5 cm long. The recrystallized compound melted sharply at 136° , which is identical with the melting point found by Woodward and Alsberg. Since none of the crystals from alcohol had any definite end faces, some of them were dissolved in acetone, in which they are very soluble, and after adding 3 volumes of chloroform, the solution was placed in the ice box to crystallize. Beautiful needle-like prisms with well developed end faces were obtained. These crystals were employed for the crystallographic work described below. An analysis for mercury gave the following result:

Subs., 0.2832 HgS, 0.1025

Calc for $(\text{CH}_3)_3\text{N.HI.HgI}_2$ Hg, 31.28 Found 31.29

Diethyl Ammonium Mercuric Iodide, $(\text{C}_2\text{H}_5)_2\text{NH.HI.HgI}_2$.—This compound was obtained in the form of a dark yellow oil by adding Mayer's reagent to a slightly acidified solution of diethyl amine. The solution was agitated while it was being cooled to 10° and the oil solidified into a bright yellow crystalline meal. This compound like the corresponding dimethyl derivative described above was found to be exceedingly soluble in alcohol and acetone and difficultly soluble in ether and chloroform. Some of the product was dissolved in acetone, and chloroform was added in a sufficient quantity to produce a slight turbidity. A gentle current of air was directed across the surface of the solution and when it became cold, due to evaporation of some of the volatile solvent, small crystals were formed. Also some well developed crystals were obtained from the aqueous solution from which the precipitated compound had been filtered by allowing it to remain for two days in the ice box. These crystals, as well as those obtained from the acetone and chloroform solution, melted at about 114° .

A series of experiments was made in order to determine how small

a quantity of diethyl amine could be detected by Mayer's reagent and it was found that no precipitate was formed when less than 4 mg. of the amine per cc. was present. An analysis gave the following results:

Subs., 0.2752: HgS, 0.0977.

Calc for $(C_2H_5)_2NH.HI.HgI_2$: Hg, 30.60. Found: 30.69

Triethyl Ammonium Mercuric Iodide, $(C_2H_5)_3NH.HI.HgI_2$.—For the preparation of this compound pure triethyl amine was made by L. Mikeska of this Bureau. A slight excess of Mayer's reagent was added to 4 g. of triethyl amine which had been acidified with hydrochloric acid and diluted to 30 cc. with water. The compound separated in the form of a dark yellow oil and solidified to a bright yellow crystalline powder when the solution was cooled to -10° . After filtering off the crystals, the filtrate was allowed to stand for two weeks in the ice box, but no further separation of crystals or oil took place. This compound was found to melt at 59 to 60° . However, it should be observed that when Mayer's reagent is added to a 0.01 *N* solution of the triethyl amine hydrochloride and allowed to remain in the ice box overnight, the compound separated in the form of very small crystals instead of an oil as mentioned above which is in agreement with the observations of Woodward and Alsberg, who first prepared it. These crystals melted at 77° to 78° . This compound is extremely soluble in alcohol and acetone and insoluble in chloroform and ether. Many experiments were made to recrystallize it but all were unsuccessful.

An analysis was made with the following results:

Subs., 0.3132: HgS, 0.1057.

Calc for $(C_2H_5)_3N.HI.HgI_2$: Hg, 29.34. Found: 29.17

Crystallography and Optical Properties.

In order to obtain means for the identification of the above described compounds, they have been submitted to detailed crystallographic and optical investigation. The crystallographic measurements were made on a Goldschmidt two-circle goniometer, and the angles are given in the coördinate system, as meridian-distance (longitude, azimuth) φ and pole-distance ρ . When an attempt was made to study the optical properties by the immersion method, the difficulty was encountered that these compounds are decomposed by all immersion liquids approaching them in refractive indices. The indices are extremely high, in the neighborhood of 1.9–2.0, and the only liquids available are solutions of metallic iodides or of arsenic sulfide in methylene iodide. Even though approximate determinations of indices were possible in some cases by working rapidly, the values obtained were too uncertain to be of any value in the practical identification of the substances, therefore, only optical properties other than indices are recorded. In fragments under the microscope the compounds all agree in being faintly yellow in color, without noticeable pleo-

chromism; and their features agree in every case with the theory for the system indicated by the crystallographic measurements.

1 : 1-Dimethyl Ammonium Mercuric Iodide, $(\text{CH}_3)_2\text{NH.HI.HgI}_2$.—The crystals of this substance obtained on allowing the mother liquor from the first crop to stand are only about 2.5 mm. in length, but are well suited to crystallographic measurement. They have the aspect of distorted square pyramids, and are often cavernous or again built up by subparallel intergrowth of several individuals. By working over the material, 6 crystals yielding fairly good reflections were finally picked out. They proved to belong to the rare class of the monoclinic system known variously as clinohedral, domatic, or No. 3. They were oriented so that the large square face became the lower base, and the two-faced form lying most nearly at right angles to this base the front unit prism. The other prominently developed two faced form then became the back upper unit pyramid, and the minute faces of other forms sometimes present had the positions of the upper base, the front clinopinacoid, and front lower unit pyramid. A diagram of a crystal exhibiting all these forms is shown as Fig. 1. Most of the crystals are bounded only by the 5 faces of C , m and p .

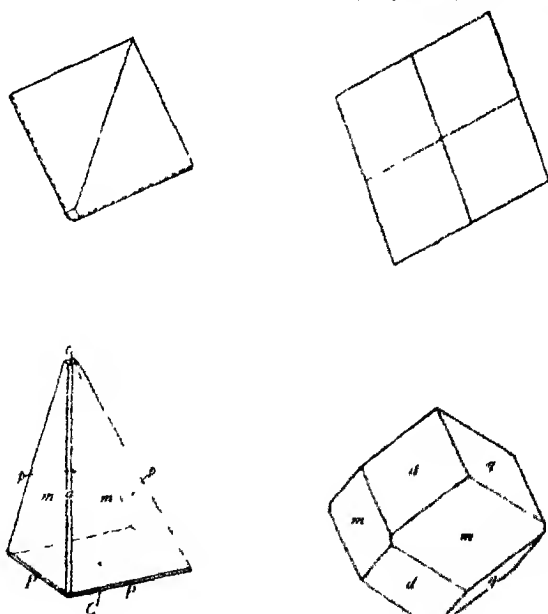


Fig. 1.

Fig. 2.

Half of the crystals were mounted with the obtuse end up, and served to measure the coordinate angles of the base and the unit prism. The balance were mounted in the opposite manner, the prism being put in

polar position, and the angles of the unit pyramid were then obtainable. The results of these measurements are presented in Table I; the probable error of the angles is about $\pm 5'$, and the axial ratio accordingly certain to 5 units in the third decimal place.

TABLE I.—ANGLES OF 1:1-DIMETHYL AMMONIUM MERCURIC IODIDE.
Monoclinic, domatic. $a : b : c = 0.9687 : 1 : 1.3406$, $\beta = 78^\circ 20'$.

Number, letter	Symbols		Description	Angles observed	
	Gdt	Mll		φ	ρ
1 <i>c</i>	0	001	Minute, rarely present	$90^\circ 00'$	$11^\circ 40'$
2 <i>C</i>	$\bar{1}0$	001	Prominently developed	$90^\circ 00'$	$11^\circ 40'$
3 <i>a</i>	000	100	Minute line face	$90^\circ 00'$	$90^\circ 00'$
4 <i>m</i>	00	110	Prominently developed	$46^\circ 30'$	$90^\circ 00'$
5 <i>p</i>	$\bar{1}1$	111	Prominently developed	$42^\circ 00'$	$61^\circ 00'$
6 <i>P</i>	11	111	Minute, rarely present	$42^\circ 00'$	$61^\circ 00'$

No other compound approaching this in composition, with which comparison of crystal form might be made, appears to have been measured, although it may be noted that a cesium mercuric iodide, with a somewhat different formula type, $2\text{CsI} \cdot 3\text{HgI}_2$, has been observed to crystallize in the same class.¹ Under the microscope double refraction is extremely strong, extinction is oblique, optical class biaxial, axial angle large, and sign negative.

1:1-Diethyl Ammonium Mercuric Iodide, $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HI} \cdot \text{HgI}_2$.—The crystals obtained from a mixture of acetone and chloroform are nearly equidimensional, with the aspect of somewhat flattened rhombic dodecahedrons. On setting up and measuring several crystals it was found that the system is rhombic, with the 3 axes not differing greatly in length, thus peri-cubic. Flattening may occur in the direction of any of the three forms present, but after a few trials the orientation of any of the crystals can be readily found. It was decided to make the axes $a > b > c$, and on this basis the following angle table has been prepared. The probable error of the angles is $\pm 2'$, and the axial ratios certain to a few units in the fourth place.

TABLE II.—ANGLES OF 1:1-DIETHYL AMMONIUM MERCURIC IODIDE
Rhombic, peri-cubic. $a : b : c = 1.1572 : 1 : 0.9102$.

Number, letter	Symbols		Description	Angles observed	
	Gdt	Mll		φ	ρ
1 <i>m</i>	00	110	All forms	$40^\circ 50'$	$90^\circ 00'$
2 <i>g</i>	01	011	equally	$0^\circ 00'$	$42^\circ 19'$
3 <i>d</i>	10	101	developed	$90^\circ 00'$	$38^\circ 11'$

There appears to be no relation whatever between the crystal form of this and the dimethyl compound, but it is interesting to compare the diethyl mercuric iodide with the corresponding chloride, which was de-

¹ Penfield, *Am. J. Sci.*, [3] 44, 311 (1892).

scribed by Topsøe¹ as rhombic pseudotetragonal (peritetragonal as here used) with $a : b : c = 0.9853 : 1.04624$. If in the present compound the a and b axes should be interchanged, and the domes taken as 021 and 201, respectively, the ratio obtained would be $0.8642 : 1.03933$, which is fairly close to the value for the chloride. The habits of the two are so different, however, that no close isomorphism is to be inferred to exist between them. Under the microscope the double refraction is extreme, extinction symmetrical, optical class biaxial, axial angle very large and sign positive.

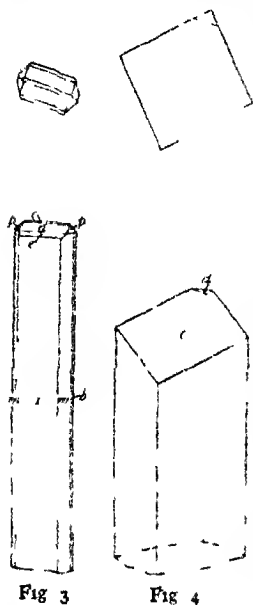


Fig 3

Fig 4

1 : 1-Trimethyl Ammonium Mercuric Iodide, $(CH_3)_3N HI HgI_2$.—The crystals obtained from alcohol consist of rods grouped into flat clusters without definite terminal planes, but from a mixture of 3 parts chloroform and one of acetone terminated needles fairly well adapted to crystallographic measurement were obtained. The results are presented in Table III, the measurements having because of the minute size of the crystals, a probable error of $\pm 5'$, so that the axial ratio is not certain beyond the third place. The prism angle deviates but a few minutes from 60° , so the substance is markedly perihexagonal.

TABLE III—ANGLES OF 1 : 1 TRIMETHYL AMMONIUM MERCURIC IODIDE
Rhombic, perihexagonal $a : b : c = 1.7262 : 1.09569$

Number, letter	Symbols		Description	Angles observed	
	Gdt	Mill		ψ	ϕ
1 c	0	001	Very narrow but definite		$0^\circ 00'$
2 b	00	010	Narrow but well marked	$0^\circ 00'$	$90^\circ 00'$
3 a	00	100	Prominent	$90^\circ 00'$	$90^\circ 00'$
4 m	0	110	The dominant form	$30^\circ 05'$	$90^\circ 00'$
5 d	10	101	The principal termination	$90^\circ 00'$	$29^\circ 00'$
6 e	20	201	A small terminal form, ρ called $47^\circ 57'$	$90^\circ 00'$	$48^\circ \approx$
7 ϕ	1	111	Minute but definite, ρ called $47^\circ 53'$	$30^\circ \approx$	$48^\circ \approx$

The chloride corresponding to this was measured by Topsøe² and found to be monoclinic, pseudo or perihexagonal with $a : b : c = 1.6165 : 1.16538$ and $\beta = 97^\circ 18'$. If the vertical axis of the iodide is doubled, the corresponding values for it are $1.7262 : 1.19138$ and $\beta = 90^\circ$. A cer-

¹ *Oversigt Danske, Videnskaberne Selskabs, Copenhagen, 1882; Z. Kryst. Mineralog.* 8, 246 (1883); and Groth's *Chem. Kryst.*, 1, 371 (1906).

² *Loc. cit.*

tain degree of similarity, though no definite isomorphism, is thus shown between the chloride and iodide compounds. Under the microscope double refraction is extremely strong, extinction is parallel, optical class biaxial, axial angle large, and sign negative.

1:1-Triethyl Ammonium Iodide, $(C_2H_5)_3N.HI.HgI_2$.—In spite of repeated trials it was found impossible to obtain well developed crystals of this compound. In the crystalline mass obtained by solidification of the oil first obtained, however, there could be found occasional individuals with definite though rough bounding planes. These yielded measurements sufficient to show the system to be monoclinic, peritetragonal although the angles were in no case measurably closer than $\approx 30'$, and the axial ratio is accordingly uncertain beyond the second place. Crystals earlier prepared by Mr. Woodward were too rounded for satisfactory measurement, but appeared to be about the same as those here described, except for tabular development on a pinacoid (*a* or *b*).

TABLE IV.—ANGLES OF 1:1-TRIETHYL AMMONIUM MERCURIC IODIDE.
Monoclinic, peritetragonal $a : b : c = 1.15 : 1 : 1.08$, $\beta = 62^\circ 30'$.

Number letter	Symbols		Description	Angles observed.	
	Gdt	Mill		ϕ	ψ
1 <i>c</i>	0	001	Chief terminations	$90^\circ 00'$	$27^\circ 30'$
2 <i>m</i>	00	110	Dominant form	$44^\circ 30'$	$90^\circ 00'$
3 <i>d</i>	-10	107	Minute	$90^\circ 00'$	$28^\circ 30'$

The chloride corresponding to this does not appear to have been prepared,¹ but it is curious to note that the form of the triethyl iodide is similar to that of the diethyl chloride compound. The latter was described as rhombic, with $a : b : c = 0.9853 : 1 : 0.4624$ but with only one face of the brachydome usually developed. If the iodide should be so oriented that the forms here taken as the base and orthodome together make up a brachydome (distorted), the axial values would be $0.98 : 1 : 0.53$. Too much significance should not, however, be attached to this similarity. Under the microscope, the double refraction is extreme, extinction oblique, class biaxial, and axial angle large.

1:1-Tetramethyl Ammonium Mercuric Iodide, $(CH_3)_4NI.HgI_2$.—Crystals of this substance prepared by Mr. Woodward several years ago, and preserved in the Bureau, were found to be minute needles, closely resembling the trimethyl compound, though differing in important respects. The system is rhombic, but the angles are perihexagonal, as in the preceding. In the present case, however, the crystals are oriented so that the front-back axis *a* is shorter than *b*, to bring out the relationship with the corresponding chloride. The angles are not measurably closer than $\approx 30'$, so that the axial ratio is uncertain beyond the second place.

TABLE V.—ANGLES OF 1:1-TETRAMETHYL AMMONIUM MERCURIC IODIDE.
Rhombic, perihexagonal $a \ b \ c = 0.59 : 1 : 0.52$

Number, letter	Symbols		Description	Angles observed	
	Gdt	Mill		α	β
1 b	000	010	Distinct	$0^\circ 00'$	$90^\circ 00'$
2 a	000	100	Distinct	$90^\circ 00'$	$90^\circ 00'$
3 m	00	110	Dominant prism form	$59^\circ 30'$	$90^\circ 00'$
4 d	10	101	Distinct	$90^\circ 00'$	$41^\circ 30'$
5 p	1	111	Chief termination	$59^\circ 30'$	$45^\circ 30'$

The tetramethyl ammonium mercuric chloride, as described by Topsøe¹ is monoclinic, but perihexagonal, its axial values not diverging much from those of the iodide $a \ b \ c = 0.5657 \ 1 \ 0.4813$ and $\beta = 93^\circ 33'$ as against $0.59 \ 1 \ 0.52$ and 90° here obtained. The two are thus isomorphous to the extent that their underlying structures are probably closely similar. The tetramethyl iodide is also close to the trimethyl iodide described previously, if the orientation is changed so that the long horizontal axis is a , then the axial ratio would become $1.60 \ 1 \ 0.88$, as against $1.73 \ 1 \ 0.96$ for the trimethyl compound. Isomorphism

is again shown here. Under the microscope double refraction is extreme, extinction is parallel, and class is biaxial, the acute bisectrix apparently running lengthwise of the needles, so that interference figures are difficult to obtain.

1:1-Tetraethyl Ammonium Mercuric Iodide, $(C_2H_5)_4NI \ HgI_2$.—The specimen of this substance prepared by Mr. Woodward, and preserved in the Bureau of Chemistry collections, proved to consist of crystals of two habits. The bulk of the material is in tabular crystals, about 0.5 mm. in diameter (Fig. 6), but scattered through these there are occasional prismatic crystals one mm. or more long, but less than 0.2 mm. thick. The angles on these two types of crystals are identical, and they evidently merely repre-

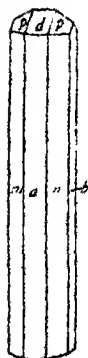


Fig. 5.

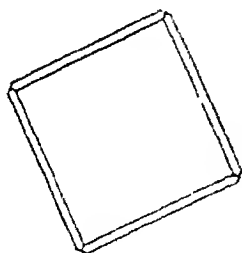


Fig. 6.

sent two crops of the same substance. The system proved to be tetragonal, with a positive axial ratio, as shown in the table, the probable error of the measurements $\pm 3'$ rendering the value of the axial ratio certain to about one unit in the third place.

¹ Loc. cit.

TABLE VI.—ANGLES OF 1 : 1-TETRAETHYL AMMONIUM MERCURIC IODIDE.
Tetragonal $a : c = 1 : 1.1577$.

Number, letter.	Symbols.		Description	Angles observed	
	Old.	Mill.		ϕ	ψ
1 <i>c</i>	0	001	Dominant form (absent on prismatic crystals)		0° 00'
2 <i>a</i>	∞ 0	100	Narrow, but always present	90° 00'	90° 00'
3 <i>m</i>	∞	110	Prominent form	45° 00'	90° 00'
4 <i>p</i>	1	111	Narrow on plates, prominent on prismatic crystals	45° 00'	58° 35'

The chloride corresponding to this in formula has been described by Topsøe¹ as triclinic, with all three axial angles near 90°, and tabular on *b*; but if the tabular form is made *c* a certain degree of resemblance is shown between the two compounds. The pole distances of forms in pyramidal positions are then 51° 04', 61° 17' and 70° 53', average 61° 05', as against the 58° 35' observed for the tetragonal pyramid on the iodide. The approach of these values is sufficiently marked to indicate at least a similarity in the structures underlying the two substances. Under the microscope the plates are practically isotropic, and in convergent light yield a uniaxial positive interference figure; and the double refraction is very strong.

Summary.

The new compounds dimethyl and diethyl ammonium mercuric iodide have been prepared and described. The amount of these compounds which can be detected by precipitation with Mayer's reagent has been determined. The crystallography and optical properties of di-, tri-, and tetramethyl and ethyl ammonium mercuric iodides have been described.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE
UNIVERSITY OF IOWA]

SOME DERIVATIVES OF *p*-DICHLOROBENZENE.¹

By JOYCE H. CROWELL AND L. CHAS. RAIFORD.

Received October 22, 1919

The use of monochlorobenzene in the manufacture of both phenol² and picric acid,³ and the fact that the preparation of the starting material always involves the production of considerable amounts of the dichlorinated compounds show that the latter are relatively plentiful by-products. In accord with the best technical practice,⁴ more than 4%

¹ *Loc. cit.*

² This report represents a part of a thesis presented by Joyce H. Crowell to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Master of Science, July, 1919.

³ *C. A.*, 11, 868 (1917).

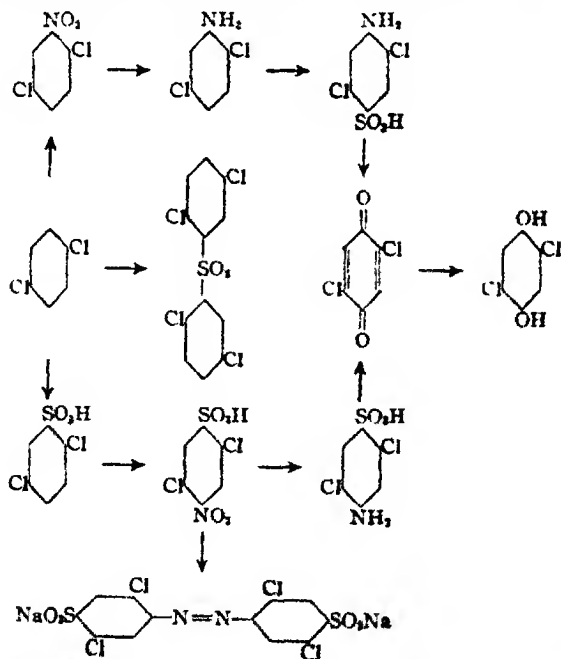
⁴ Marshall, *Explosives*, 1, 278 (1917).

⁵ Ullman, *Encyclop. tech. Chem.*, 11, p. 370.

of the benzene used for this work is converted into *p*-dichlorobenzene, which is said to have practically no industrial value except that *p*-phenylenediamine¹ can be produced from it on a semi-technical scale. It seemed, therefore, a matter of interest to study more carefully than had been done before some of the derivatives of *p*-dichlorobenzene.

Among the reactions that suggested themselves in this connection, the following were considered (a) The removal of one or both chlorine atoms and their replacement by hydroxyl or other radicals; (b) the preparation of some of the possible nitrosulfonic acids and their derivatives.

To secure material for the work indicated it was necessary to prepare a quantity of the well-known mononitro compound, 2,5-dichloronitrobenzene, for which we have determined the optimum conditions and recorded the yield.² This material was reduced to 2,5-dichloroaniline, which was then sulfonated in accordance with the method of Noelting and Kopp,³ after which the acid (or its sodium salt) was oxidized to 2,5-dichloroquinone, and the latter reduced to its hydroquinone, in order to secure material with which to compare the derivatives of our new nitro-



¹ *Chem. Centr.*, 1908, II, 1221.

² Though this compound has been prepared by several chemists, no one whose data is accessible to us has recorded either the yield or the details of the method by which the maximum yield can be obtained.

³ *Ber.*, 38, 3513 (1905).

sulfonic acid (see experimental part). This was obtained through the nitration of 2,5-dichlorobenzene sulfonic acid, which was prepared by Holleman and van der Linden's method¹ modified in such a way as to enable us to isolate and recognize as 2,2'-5,5'-tetrachloro-diphenylsulfone, the insoluble body mentioned but not isolated by Lesimple.² The identity of this acid was established by the study of several of its salts and other derivatives, while its constitution was determined by the reduction of its sodium salt and the oxidation of the corresponding amino compound to 2,5-dichloroquinone. These reactions may be briefly indicated by the formulas given above.

Experimental.

Starting Material.—The *p*-dichlorobenzene with which this research was begun was obtained from the Dow Chemical Company, and consisted of white, massy, transparent crystals that melted sharply at 53°.³ It was free from the *ortho* and *meta* isomers, which are liquids at ordinary temperatures, and was used without further purification.

Nitration of *p*-Dichlorobenzene.—The mononitro compound was obtained in almost theoretical yield by a modification of the method published by Morgan,⁴ special care being taken to avoid the formation of isomers⁵ through the introduction of more than one nitro group. We found it more satisfactory to add the mixed acids in 4 or 5 portions during half an hour, and to shake the flask during the entire period, after which the mixture was heated for an hour or so on the water bath. The product was separated and purified in the usual manner, and had the melting point and other properties recorded by Morgan.

The Sulfonation of *p*-Dichlorobenzene.—Lesimple⁶ studied the action of sulfuric acid on a dichlorobenzene, evidently the *para* compound, as early as 1868, and described a dichloro-benzenesulfonic acid and several of its salts. Beilstein and Kurbatow⁷ found later that *p*-dichlorobenzene reacts with sulfuric acid with much difficulty, and then only incompletely

¹ *Rec. trav. chim.*, 30, 305 (1911).

² *Bull. soc. chim.*, [2] 10, 266 (1868).

³ All melting points reported in this paper are uncorrected.

⁴ *J. Chem. Soc.*, 81, 1382 (1902).

⁵ Morgan found that the introduction of a second nitro group gave two isomers, 2,5-dichloro-1,4-dinitrobenzene and 2,5-dichloro-1,3-dinitrobenzene, and that the first was formed in largest amount, though he did not record the yield of either. Hartley and Cohen (*J. Chem. Soc.*, 85, 865 (1904)), also, found that two isomers were formed, and that the quantity of the *meta* compound (the second one named above) was about 6 times that of the *para* isomeride, but no yields were given; while Nason (*THIS JOURNAL*, 40, 1602 (1918)) has recently found that when two nitro groups are introduced the product is a mixture of all 3 of the possible isomers. The relative yields were determined, the *para* compound being present in largest amount.

⁶ *Loc. cit.*

⁷ *Ber.*, 7, 1760 (1874).

even after long heating in a sealed tube at 230° , using massy, fuming acid, while Holleman and Van der Linden¹ state that sulfuric acid containing more than 0.3% of free sulfur trioxide will sulfonate it. For more satisfactory results they recommend an acid containing 10% sulfur trioxide, at ordinary temperature, and acting for 24 hours' time. We obtained the highest yields of product by the use of an acid containing 10-12% of sulfur trioxide, when the reaction was carried out as follows: A mixture of 150 g. of dichlorobenzene and 225 g. of the sulfuric acid specified was placed in a suitable flask and heated to $140-150^{\circ}$, while the material was kept in constant motion with a mechanical stirrer. After about 45 minutes the two layers had disappeared and the mixture, which was quite dark in color, was cooled somewhat and poured into a large volume of cold water. This caused the separation of any unchanged material present together with some of the tetrachloro-diphenylsulfone already referred to. About 35 g. of solid was filtered off at this point and the filtrate concentrated, after which, upon cooling, the sulfonic acid separated out in long, colorless needles. Recrystallization from water removed practically all the sulfuric acid. A yield of 85-90% was obtained. A second portion of the sulfonic acid solution, prepared as indicated above, was poured into saturated salt solution, and the sodium sulfonate precipitated out. On recrystallization from hot water this separated out in glittering, hexagonal plates, or in long, silky needles. The plates contained one molecule of water of crystallization, and had a tendency toward efflorescence. A sample heated to constant weight at 110° gave the following figures:

Subs., 0.5233: H_2O , 0.0338

Calc. for $C_6H_2Cl_4SO_3Na \cdot H_2O$ H_2O , 6.74 Found 6.46

2,2'-5,5'-Tetrachloro-diphenylsulfone, $(C_6H_2Cl_4)_2SO_2$. In his report on the sulfonation of *p*-dichlorobenzene, Lesimple¹ refers to an insoluble product that separated as the reaction proceeded, and suggested that this might be a sulfobenzid, though he did not purify the material or study it further. In our work about 30 g. of this substance was formed during the sulfonation of 150 g. of dichlorobenzene. The product is not very soluble in cold alcohol, but much more soluble in the hot liquid, out of which, on cooling, it crystallizes in colorless, small, thick, diamond-shaped crystals whose sides are parallelograms. It is quite soluble in hot benzene, and insoluble in water. It melts at 179° . Analysis for halogen gave figures that agree with the formula assigned.

Subs., 0.5262 AgCl (Carius), 0.8438.

Calc. for $(C_6H_2Cl_4)_2SO_2$ Cl, 39.84. Found 39.67

2,5-Dichloro-4-nitrobenzene-sulfonic Acid, $C_6H_2Cl_2NO_3SO_3H$.—So far as far as we are aware no mononitrosulfonic acid derived from *p*-dichloro-

¹ *Loc. cit.*

benzene has heretofore been reported in the literature, although similar derivatives from the *ortho* and *meta* isomers are known¹. On this account it seemed a matter of interest to us to investigate the action of fuming nitric acid on 2,5-dichloro-benzenesulfonic acid. It may be stated here, at once, that this is probably the only method by which a nitrosulfonic acid can be prepared from the *para* isomer. for all attempts to sulfonate 2,5-dichloro-nitrobenzene were unsuccessful. Many experiments with varying concentrations of acid showed that no sulfonation took place below 150°, but above that temperature violent decomposition, with almost complete carbonization, occurred. The action of fuming nitric acid alone or in the presence of sulfuric acid gave, under the conditions we imposed, a mononitrated product. A quantity of the sulfonic acid weighing about 75 g. was treated with a mixture of 54 cc. of nitric acid (sp. gr. 1.6) and 32 cc. of sulfuric acid (sp. gr. 1.84). Such a mixture approximates that one found by Saposchinikoff² to have the maximum vapor pressure which, according to his results, contains nitric acid, sulfuric acid and water very nearly as represented by the formula $5\text{HNO}_3 \cdot 2\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. The reaction mixture was then boiled down until a sample crystallized on cooling. This compound was also prepared by mixing 35 g. of the sulfonic acid with 50 cc. of nitric acid (sp. gr. 1.6), and then concentrating the mixture until a sirupy condition was produced. On standing for a day or two this liquid deposited bushy, burr-like crystals composed of flat, yellow needles. Repeated crystallization from water gave a compound that is quite hygroscopic and apparently has a melting point near 150°. The acid is not soluble in organic solvents to any appreciable degree, and this behavior, in addition to the properties already named, has prevented the preparation, thus far, of a perfectly pure sample of our product. Nevertheless, since several of its salts and other derivatives have been prepared and analyzed, the composition and structure of the acid are fixed without doubt.

The Salts of 2,5-Dichloro-4-nitrobenzene-sulfonic Acid, $\text{C}_6\text{H}_2\text{Cl}_2\text{NO}_2\text{SO}_3\text{Me}$.

The Sodium Salt, $\text{C}_6\text{H}_2\text{Cl}_2\text{NO}_2\text{SO}_3\text{Na}$.—This compound was prepared by salting out the nitration mixture, and also by nitration of the sodium salt of the sulfonic acid. A quantity of the sodium salt weighing about 50 g. was mixed with 50 cc. of fuming nitric acid (sp. gr. 1.6), and heated for several hours under a return condenser, after which 40 cc. more of the acid was added and the heating continued for some time. On evaporating off the excess of nitric acid the sodium nitrosulfonate was left as a pale yellow, amorphous powder. It was purified by recrystallization

¹ *Chem. Centr.*, 1906, II, 1537; *Ibid.*, 1908, I, 726.

² *J. Russ. Phys. Chem. Soc.*, 36, 518 (1904); *J. Chem. Soc. Abs.*, 86, II, 538 (1904). We regret that the original of this paper was not accessible to us.

from water, from which it separated in thin, wing-like scales or leaflets that showed a tendency to clump together, and contained one molecule of water of hydration. It is not easily soluble in organic solvents. By the second method indicated about 90% of the salt was nitrated. Analyses for water of hydration for halogen and for sodium gave results that are in agreement with the requirements of a mononitro compound.

Subs, 2.5005, 0.8124 H_2O , 0.1386, 0.0455
 Subs, 0.5464 $AgCl$ (Carius), 0.5434
 Subs, 0.8273, Na_2SO_4 , 0.2013
 Calc. for $C_6H_2Cl_2NO_2SO_3Na \cdot H_2O$ H_2O , 5.77, Cl , 24.12, Na , 7.82 Found H_2O , 5.54, 5.61, Cl , 24.57, Na , 7.87

With the exception of the first analysis for water the analyses here recorded were made upon portions of the same sample

The Potassium Salt, $C_6H_2Cl_2NO_2SO_3K$.—This substance was prepared by salting it out from a saturated solution of potassium chloride, by addition of the free nitro acid, in the manner used to obtain the sodium salt. The product has practically the same solubilities as the sodium salt, crystallizing out of water in pale yellow, flat, bushy needles that tend to cluster in the form of nodules containing one molecule of water of hydration. Analyses for water and for potassium gave the following figures:

Subs, 1.0454 H_2O , 0.0553
 Subs, 0.7354 K_2SO_4 , 0.2081
 Calc. for $C_6H_2Cl_2NO_2SO_3K \cdot H_2O$ H_2O , 5.47, K , 12.61 Found H_2O , 5.29, K , 12.69.

The Ammonium Salt, $C_6H_2Cl_2NO_2SO_3NH_4$.—This salt was prepared by the addition of aqueous ammonia in excess to the solution of free nitro acid, and concentration of the resulting liquid. The product was further purified by crystallization from water from which it separated in lemon-yellow tufts of flat, grass-like needles, sometimes clustering together to form hard balls. It is easily soluble in water. Analysis for the ammonium radical gave results that agree with the formula assigned.

Subs, 0.7552 NH_3 , 0.0446
 Calc. for $C_6H_2Cl_2NO_2SO_3NH_4$ NH_3 , 5.88 Found 5.91

The Barium Salt, $(C_6H_2Cl_2NO_2SO_3)_2Ba$.—This compound was made by the action of barium nitrate on the sodium salt, and was obtained as a precipitate by mixing solutions of these salts. It is but sparingly soluble in water, and from a hot solution it separates, upon cooling, in the form of thin, sharp-pointed leaflets having the appearance of peach leaves, and clustering together in roset-like forms. It was analyzed for barium.

Subs, 0.2553 $BaSO_4$, 0.0882
 Calc. for $(C_6H_2Cl_2NO_2SO_3)_2Ba$; Ba , 20.22. Found: 20.32.

Proof of the Constitution of the Acid, $C_6H_2Cl_2NO_2SO_3H$.—A portion of the sodium salt was reduced with tin and hydrochloric acid in the

usual manner, and the resulting sodium dichloro-sulfanilate crystallized from the mixture. It separated in the form of colorless, shining leaflets. Its water solution turned red slowly on standing exposed to the air. Analysis for halogen gave results consistent with the formula below.

Subs., 0.4230. AgCl (Carius), 0.4600

Calc. for $C_6H_2Cl_2NH_2SO_3Na$ Cl, 26.85 Found 26.89

This compound was further identified by the preparation of its acetyl derivative, which was carried out by heating the salt with acetic anhydride in the usual way. The product is easily soluble in water, from which it was crystallized in the form of colorless masses made up of long, thin needles having the appearance of cotton. A determination of nitrogen gave the following figures:

Subs., 0.2985 6.95 cc; HCl, 0.1427 N

Calc. for $C_6H_2Cl_2SO_3NaNHCOCH_3$, N, 4.58 Found. 4.65

The relative positions of the nitro and sulfonic acid groups in the acid under consideration were determined by oxidation of the sodium salt of the corresponding amino compound. Five g. of this product, purified as indicated above, was slowly mixed with a solution containing 9 g. of sodium dichromate dissolved in 35 cc. water and 14 cc. of conc. sulfuric acid dissolved in 80 cc. water. The temperature was kept below 10° , and the mixture was constantly agitated by means of a mechanical stirrer. The resulting quinone separated in the form of yellow needles which, after recrystallization from alcohol, melted sharply at 160° . To show that in this compound the chlorine atoms occupy Positions 2 and 5, and that the substance in hand was identical with 2,5-dichloroquinone, obtained by Noetting and Kopp,¹ a sample of the latter was prepared by the method described by these chemists. This product, also, melted at 160° , and a mixture of it and the quinone obtained by the oxidation of our sulfanilic acid melted at the same temperature as either of them separately, which indicates their identity. The nitro and the sulfonic acid groups in our new acid are, therefore, in the *para* positions with respect to each other.

Sodium Salt of 2,2'-5,5'-Tetrachloro-azobenzene-4,4'-disulfonic Acid, $(SO_3NaC_6H_2Cl_2)_2N_2$.—This was formed by the alkaline reduction of the sodium salt of the nitrosulfonic acid, and also by reduction in weakly acid solution. Ten g. of the recrystallized sodium salt was mixed with a solution of sodium hydroxide containing one g. of the alkali in 10 cc. of water, and this was treated with 15 g. of zinc dust, added in 3 portions. The mixture was warmed and the reaction completed by boiling until the liquid became faintly brown or nearly colorless. On filtering it rapidly turned red, and dark brownish red on boiling. When the solution had become very dark colored and no further change seemed to take

¹ *Loc. cit.*

Preparation of the Oil.—The oil was expressed in January, 1918, by means of an oil expeller, under the supervision of Mr. H. S. Bailey, formerly in charge of this laboratory, who also refined a portion. The oil was stored at room temperature until May, 1919, before an opportunity was found for making an examination of it.

Physical and Chemical Examination.—The crude oil has a yellow color in thin layers and a brownish red color in layers of moderate thickness, while the refined oil is yellow with a red tinge. Both crude and refined oils have a bland, fatty taste and a fatty odor. The physical and chemical characteristics are given in Table I. The percentages of saturated and unsaturated acids were determined on the refined oil. For all other determinations reported in Col. I crude oil was used. The low Reichert-Meissl and Polenske numbers indicate the almost complete absence of glycerides of volatile acids. Only 0.33% of acids soluble in water was found. The acetyl value, 27.8, indicates a small amount of glycerides of hydroxylated acids. The keeping quality of the oil is very good as shown by the low acid value, and also by the absence of a rancid taste or odor. The percentage of insoluble acids, 94.66, has been corrected for unsaponifiable matter and represents the actual amount of insoluble acids and not insoluble acids + unsaponifiable matter (Henner number), which is sometimes reported.

TABLE I.—HUBBARD SQUASH SEED OIL.
Physical and Chemical Characteristics

	Oil	Insoluble acids	Liquid acids	Solid acids.
Specific gravity 25°/25°	0.9179	
Refractive index 25°	1.4714	
Iodine number (Hanus)	121.0		151.2	3.8
Saponification value	191.5	201.8	201.7	210.3
Mean molecular weight		278.0	278.1	266.8
Reichert-Meissl number	0.37			
Polenske number	0.39			..
Acetyl value	27.8			
Acid value	0.50			..
Unsaponifiable matter, %	1.06			..
Soluble acids, %	0.33
Insoluble acids, %	94.66
Unsaturated acids, %	76.45			..
Saturated acids, %	18.37			..
Titer		29.8° to 29.85°		

Since the percentages of saturated and unsaturated acids were determined on the refined oil the influence of the unsaponifiable matter was to some extent eliminated. The mean molecular weight of the saturated acids, 266.8, indicates a mixture of palmitic acid (m. w. 256.3) and stearic acid (m. w. 284.4). The mean molecular weight of the unsaturated acids, 278.1, is slightly lower than either oleic acid (m. w. 282.4) or linolic acid (m. w. 298.4).

The Renard test for arachidic acid gave a precipitate, the weight of which was equivalent to 5.6% of the oil. However, after several recrystallizations from 95% alcohol the melting point of this precipitate was found to be 68.5–69°, indicating stearic and not arachidic acid.

Examination of the Unsaturated Acids.—The unsaturated acids were separated by the lead salt-ether method and dried in a current of carbon dioxide. The bromine addition derivatives were then made and separated according to the method of Eibner and Muggenthaler.¹ To the unsaturated acids dissolved in dry ether and cooled to –10° bromine was slowly added. The mixture was then allowed to stand for two hours at –10°. The ethereal solution contained no precipitate, showing the absence of linolenic acid since linolenic hexabromide is insoluble in ether. The excess bromine was then removed by washing in a separatory funnel with an aqueous solution of sodium thiosulfate. The ethereal solution was dried with anhydrous sodium sulfate, filtered into a flask and the ether distilled off, after which the residue was boiled with petroleum ether. Oleic dibromide is very soluble in petroleum ether while linolic tetrabromide is soluble with difficulty. After standing in the ice-chest overnight the insoluble tetrabromide was filtered off. The filtrate was evaporated to dryness, dried in a vacuum oven and weighed. The bromine content was then determined by boiling a small sample of the residue with conc. nitric acid and solid silver nitrate. Oleic dibromide contains 36.18% of bromine and linolic tetrabromide contains 53.33%. Therefore, knowing the bromine content of the residue, it is possible to calculate the proportions of dibromide and tetrabromide present. The data obtained upon examining the unsaturated acids are given below

Sample of unsaturated acids	3 7335 g.
Linolic tetrabromide insoluble in petroleum ether, m p 113–114°	4 4076 g.
Residue (dibromide and tetrabromide)	4 8237 g.
Bromine content of residue	43 65%
Dibromide in residue 56 44% or	2 7225 g.
Tetrabromide in residue 43 56% or	2 1012 g.
Total tetrabromide found	6 3088 g.
Linolic acid equivalent to tetrabromide 2 0568 g or	55.09%
Oleic acid equivalent to dibromide 1 7370 g or	46.49%

The percentages of linolic and oleic acids in the unsaturated acids are converted into percentages of glycerides in the original oil as follows:

	Found. %	Calculated to basis of 100%	Original oil, %.	Glycerides in original oil. %
Oleic acid ..	46 49	45 77	34.99	36 56
Linolic acid .	55 09	54.23	41 46	43.34
Total.....	101 58	100 00	76 45	79.90

¹ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 2, 5th Ed., 568–578.

Examination of Saturated Acids.—The saturated acids were separated from the unsaturated acids by the lead salt ether method. The methyl esters were prepared and subjected to fractional distillation under diminished pressure. The temperatures and pressures during distillation and the weights of the fractions are given in Table II. The iodine numbers and saponification values of the various fractions were determined and the mean molecular weights calculated, using 56.1 as the molecular weight of potassium hydroxide. These results are contained in Table III. The molecular weight of methyl palmitate is 270.3 and of methyl stearate 298.4. The molecular weights of the 5 fractions lie between these two values and indicate mixtures of palmitate and stearate. The molecular weight of the residue is greater than that of methyl stearate and indicates, therefore, an ester of an acid of greater molecular weight than stearic.

TABLE II.
Fractional Distillation in Vacuum of Methyl Esters of Saturated Acids,
46.8 g. Ester Subjected to Distillation.

Fractions	Temperature Degrees	Pressure Mm	Weight of fraction, G.
1...	178-181	7	22.6
2.	182-184	6.5	10.2
3	185 rose quickly to 187, 187-189	6.5	6.05
4	189-195	5.5	5.85
5	196 rose quickly to 210, 210-224	6.0	1.15
Residue.....			0.80
Total...			46.65

TABLE III.
Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated
Acids.

Frac- tion.	Iodine No.	Saponi- fication value.	Mean molecular weight.	Palmitic acid.		Stearic acid.		Arachidic acid		Unsat'd acids.	
				%.	G.	%.	G.	%	G.	%	G.
1.....	1.6	206.0	272.3	87.76	19.82	6.04	1.36	.	.	1.06	0.24
2.....	2.7	199.9	280.6	59.60	6.08	33.60	3.43	.	.	1.79	0.18
3.....	3.8	195.3	287.2	36.79	2.23	55.82	3.38	.	.	2.50	0.15
4.....	4.7	191.6	292.8	17.63	1.03	74.49	4.38	.	.	3.10	0.18
5.....	6.3	189.1	296.6	5.80	0.07	85.30	0.98	.	.	4.17	0.05
Residue	19.7	187.5	299.2	.	.	75.94	0.60	6.36	0.05	13.02	0.10
Total.					29.23		14.13		0.05		0.90

The free acids recovered from Fraction 5 and from the residue, were fractionally crystallized from 95% alcohol, and the melting points determined with the following results:

Fraction 5.	M. p.
1st crystallization from alcohol.....	64-65°
2nd crystallization from alcohol.....	65-67°
3rd crystallization from alcohol.....	67-68°

The last crop of crystals was too small for further recrystallization. Since stearic acid melts at 69° this fraction apparently did not contain an acid higher than stearic.

Residue	M p
1st crystallization from alcohol	$70-71^{\circ}$
2nd crystallization from alcohol	$76-77^{\circ}$

The melting point of arachidic acid is 77° . This last crop of crystals after drying, weighed 0.1047 g. It was subjected to combustion analysis with the following results

Calc. for arachidic acid C, 76.85 H 12.91 Found¹ C, 76.71, H, 13.22.

This is conclusive evidence of the presence of arachidic acid.

The percentages and weights of unsaturated, palmitic, stearic and arachidic acids present in the various fractions and in the residue have been calculated with the results given in Table III. The various steps in the calculation of Fraction 1 are given below in order to illustrate the method.

$278.1 =$ mean molecular weight of unsaturated acids

$278.1 + 14 = 292.1$ mean molecular weight of methyl esters of unsaturated acids

$56.1 =$ molecular weight of potassium hydroxide

$\frac{56.1}{292.1} \times 1000 = 192.1 =$ saponification value of methyl esters of unsaturated acids.

$151.2 =$ iodine number of unsaturated acids

$\frac{278.1}{292.1} = \frac{x}{151.2} \quad x = 144.0 =$ iodine number of esters of unsaturated acids

$\frac{16 \times 100}{144.0} = 11.1 =$ percentage of esters of unsaturated acids

$100 - 11.1 = 88.9 =$ percentage of esters of saturated acids

$0.0111 \times 192.1 = 2.1 \text{ mg} =$ potassium hydroxide required to saponify unsaturated esters in one gram of fraction

$206.0 - 2.1 = 203.9 \text{ mg}$ potassium hydroxide required to saponify saturated esters in one gram of fraction

$203.9 + 988.9 = 206.2$ saponification value of saturated esters

$56.1 + 206.2 = 272.1$ mean molecular weight of saturated esters

Using the molecular weights of methyl palmitate (270.3) and methyl stearate (298.4) the data below are calculated

	% of saturated acids	% of fraction	% of free acids in fraction
Methyl palmitate	93.59	92.55	87.76
Methyl stearate	6.41	6.34	6.04
Methyl esters of unsaturated acids		1.11	1.06
Total	100.00	100.00	94.86

The data in Table III are summed up in Table IV and the percentages of glycerides in the original oil calculated. It will be noted that the calculated amount of arachidic acid in the residue is only 0.05 g., whereas we were able to crystallize out 0.1047 g. The residue was very highly

¹ Analysis by Chas. E. F. Cersdorff.

colored and this interfered with the accuracy of the determination of the saponification value. There was at least, therefore, 0.1047 g. of arachidic acid in the residue and this is equivalent to 0.04% of the glyceride in the original oil.

TABLE IV.
Composition of Saturated Acids.

	G	%	% of original oil	% of glycerides in original oil.
Palmitic acid...	29 23	65 97	12 12	12 73
Stearic acid	14 13	31.89	5 86	6 12
Arachidic acid	0 05	0 11	0 02	0 02
Oleic acid	0 90	2 03	0 17	0.18
Linolic acid			0 20	0 21
Total	44 31	100 00	18 37	19 26

Summary.

The chemical and physical characteristics of a sample of cold pressed Hubbard squash seed oil have been determined. An exhaustive study has been made of the composition of the oil, the results of which are given in the following table:

		%
Glycerides of	Palmitic acid.	13
	Stearic acid	6
	Arachidic acid, trace about.	0 04
	Oleic acid	37
	Linolic acid	44
Unsapönifiable matter.		1

WASHINGTON, D. C.

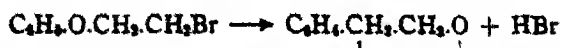
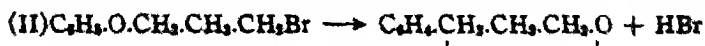
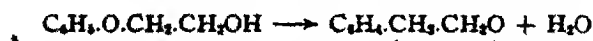
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SYNTHESES OF CHROMANES AND COUMARANES. II.

By R. E. RINDFUSZ, P. M. GINNINGS AND V. L. HARNACK.

Received November 4, 1919.

In a previous article¹ it was shown that chromane and coumarane may be easily prepared by either of two methods:



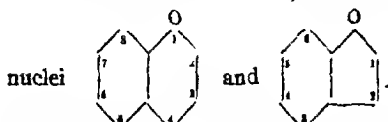
The procedure in each case is to heat the hydroxy or bromo ether with zinc chloride. The same products may also be obtained by heating free

¹ THIS JOURNAL, 41, 665 (1919).

phenol with ethylene or trimethylene chlorohydrin, but the yields are very low.

It was pointed out that, since phenol forms the starting point in each case, it should be possible by using substituted phenols to prepare various derivatives of the chromanes and coumaranes. The object of the present research was to make such compounds, as well as to compare and to improve the methods already given.

The system followed in naming the substituted chromanes and coumaranes is that of Stoermer,¹ numbering the positions on their respective



The inconsistency of starting to number from the oxygen in chromane and from the α -carbon in coumarane is obvious, and since there can be no substitution on the oxygen, the second plan seems preferable. However, these two methods are already in use² and analogous systems are employed for coumarin,³ for γ benzo-pyrone (chromone)⁴ and for benzo furane (coumarone).⁵ So it seems best not to attempt a change.

During the course of this investigation it was found that phosphorus pentoxide could be used to dehydrate the hydroxy-ethyl or hydroxy-propylphenyl ether instead of the zinc chloride as in the reactions indicated above. The products in each case are the same. This reagent does not affect the halogen substituted ether as does the zinc chloride. Thus it is shown that the closing of the ring is a simple dehydration between the hydroxy group of the side chain and the hydrogen of the ring, and is not a substitution of halogen followed by elimination of halogen acid, as was suggested as a possibility in the first paper.

The yields by the phosphorus pentoxide dehydration are better than those by either method using the zinc chloride and the procedure rather more simple since there is not the tendency for carbonization. In general, the reaction is carried out as follows: The hydroxy ether to be dehydrated is dissolved in some inert solvent as toluene or ethyl methyl ketone which will allow refluxing at a fairly high temperature and still be easily fractionated from the cyclic ether which is to be prepared. Then phosphorus pentoxide is added in small quantities, allowing one molecule of the dehydrating agent for two molecules of the water to be taken up. The flask is frequently shaken, since at first there is a tendency to cake.

¹ *Ber.*, 36, 2872-2877 (1903).

² *Richter, Lexikon*, 1, 17-18.

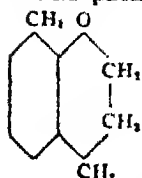
³ *C. A.*, 12, 2985 (1918). (Index.)

⁴ *C. A.*, 11, 3769 (1917). (Index.)

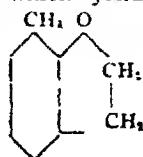
⁵ *C. A.*, 12, 2941 (1918). (Index.)

In some cases, the order is reversed, the phosphorus pentoxide being suspended in the solvent and the hydroxyether run in. The mixture is refluxed for about an hour, and then most of the solvent is distilled off. The remaining liquid when cool is poured from the mass of phosphorus compounds at the bottom of the flask, ether is added and the solution washed with alkali and with water. After drying with calcium chloride, the ether is evaporated and the product distilled. This method was not discovered until the work was well under way and not all of the preparations previously carried out were repeated. However, each method was used in enough experiments to demonstrate clearly the superiority of this one.

The phenols used are (1) *o*-cresol which yields 8-methylchromane,

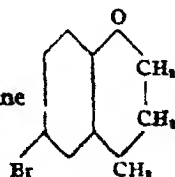


and 6-methylcoumarane,

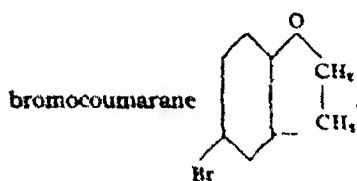


(2) *p*-Bromophenol

which gives as final products 6-bromochromane



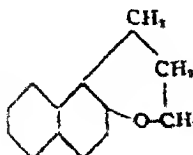
and 4-



bromocoumarane

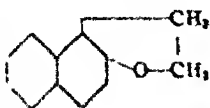
(3) β -naphthol which allows the pre-

paration of β -naphtho-dihydro-pyrane



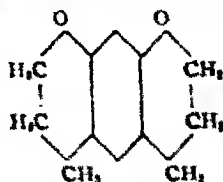
and β -naphtho-

dihydro-furane

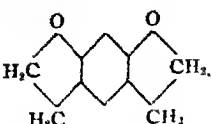


and (4) resorcinol which gives sym-

metrical benzo-tetrahydro-dipyrane,



and symmetrical

benzo-tetrahydro-difurane, . An attempt was made to

prepare the derivatives from *p*-nitrophenol. γ -Hydroxypropyl-*p*-nitrophenyl ether is easily prepared by refluxing the phenol with trimethylene chlorohydrin in the presence of sodium carbonate. On attempting the dehydration with either zinc chloride or phosphorus pentoxide, a violent reaction takes place and the whole goes almost instantly to tars and carbon.

Further investigations are being carried on to study the applicability of these reactions to the preparation of various cyclic compounds.

Experimental Part.

Derivatives of *o*-Cresol.

γ -Hydroxypropyl-*o*-tolyl Ether, $C_8H_7(CH_3)(O-CH_2CH_2CH_2OH)^2$.—Sodium was dissolved in absolute alcohol and the theoretical quantity of *o*-cresol added. Following this the mixture was treated with an equimolecular amount of trimethylene chlorohydrin and refluxed on the steam bath for about two hours. Most of the alcohol was then distilled off and the residue diluted with water. The product was extracted with ether, washed with sodium hydroxide and with water, and dried over potassium carbonate and distilled. The ether was obtained in 65% yield as a colorless oil boiling at $174-176^\circ$ at 42 mm; n_D^{27} , 1.523, d_{20} , 1.053.

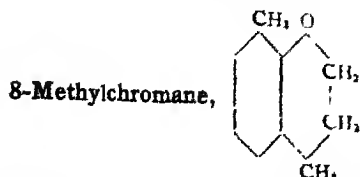
Subs., 0.2864; C, 61.45%; H, 6.90%; O, 31.7%; Found, 71.3 mm.

Calc. for $C_{11}H_{15}O_2$: C, 72.1; Found, 71.9.

γ -Bromopropyl-*o*-tolyl Ether, $C_8H_7(CH_3)(O-CH_2CH_2CH_2Br)^2$.—Twenty-three g. of sodium was dissolved in 200 cc. of absolute alcohol and 108 g. of *o*-cresol added. This was then refluxed for two hours with twice the molecular amount, 405 g., of trimethylene bromide. After this the mixture was treated as was the hydroxy ether above. The product which was fractionated from the excess trimethylene bromide was a clear oil with a rather fragrant odor and boiled at $154-6^\circ$ at 20 mm. Yield, 25%; n_D^{27} , 1.535, d_{20} , 1.299.

Subs., 0.2816; AgBr, 0.2280.

Calc. for $C_{10}H_{13}OBr$: Br, 34.9; Found, 34.5.



(1) Preparation from γ -bromo-

propyl-*o*-tolyl ether. 50 g. of the ether just described was heated

under a reflux with 5 g. of anhydrous zinc chloride. Copious fumes of hydrogen bromide were given off. After about half an hour the material was allowed to cool, and was then taken up in ether, washed with alkali and with water and dried over calcium chloride. The product distilled at 114° to 116° at 20 mm., and was a colorless oil with an odor very like cresol; n_D^{27} , 1.542; d_{20} , 1.039.

Subs., 0.3716. CO_2 , 623.1 cc. (24° , 747 mm.).

Calc. for $C_{10}H_{10}O$: C, 81.1. Found: 81.4.

(2) Preparation from γ -hydroxypropyl-*o*-tolyl ether and zinc chloride. γ -Hydroxypropyl-*o*-tolyl ether was refluxed with $\frac{1}{10}$ its weight of anhydrous zinc chloride. The temperature rose to 235° and then dropped gradually to 180° where it remained constant. The product was then fractionally distilled in 10 to 15% yield.

(3) Preparation from γ -hydroxypropyl-*o*-tolyl ether and phosphorus pentoxide. Forty g. of phosphorus pentoxide was suspended in 200 cc. of dry benzene and 100 g. of the hydroxy ether slowly added with shaking. After refluxing for a short time, the mixture was poured from the phosphorus compounds and distilled. The product may be washed with alkali and with water and redistilled with very little loss. An excellent grade of material practically all boiling at 114 – 115° at 20 mm. was obtained in 76% yield.

(4) Preparation from *o*-cresol, trimethylene chlorohydrin and zinc chloride. 64 g. of trimethylene chlorohydrin, 74 g. of *o*-cresol and 5 to 10 g. of zinc chloride were heated together under a reflux condenser until the temperature became practically constant. After taking up in ether and washing with alkali, and with water, the mixture was fractionated giving 2 to 5% yields.

β -Hydroxyethyl-*o*-tolyl Ether, $C_6H_4(CH_3)(OCH_2CH_2OH)^2$.—This was prepared exactly as the γ -hydroxypropyl-*o*-tolyl ether described above by substituting ethylene chlorohydrin for the trimethylene compound. The clear colorless product boils at 143 – 145° at 20 mm. Yield, 72%; n_D^{27} , 1.528; d_{20} , 1.079.

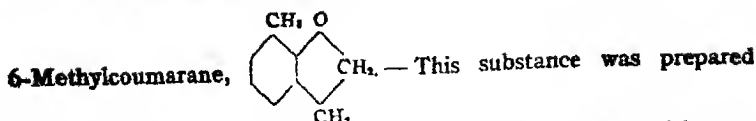
Subs., 0.4700; CO_2 , 750.0 cc. (30.9° , 739.1 mm.).

Calc. for $C_8H_{10}O_2$: C, 71.05. Found: 71.25.

β -Bromoethyl-*o*-tolyl Ether, $C_6H_4(CH_3)(OCH_2CH_2Br)^2$.—The directions given above for γ -bromopropyl-*o*-tolyl ether were followed in this preparation, ethylene bromide being substituted for trimethylene bromide. The product is a sweet-smelling, colorless liquid boiling at 133 – 4° at 20 mm. Yield, 40%; n_D^{27} , 1.544; d_{20} , 1.360.

Subs., 0.4902; AgBr, 0.4332.

Calc. for $C_8H_{10}OBr$: Br, 37.2. Found: 37.4.



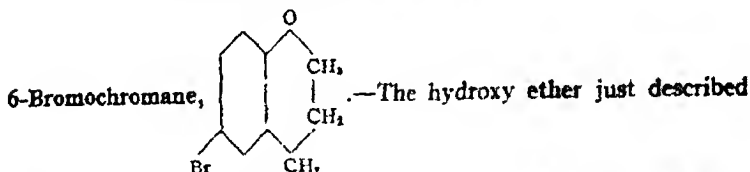
by each of the methods given above for 8-methylchromane with very similar yields in each case. The dehydration of β -hydroxyethyl-*o*-tolyl ether by the use of phosphorus pentoxide gave a 50% yield. The compound is a colorless liquid boiling at 119–120° at 65 mm.; n_D^{27} , 1.527; d_{20} , 1.000.

Subs., 0.2258 CO₂, 377.2 (24°, 747 mm.)
Calc. for C₉H₁₀O C, 80.6 Found 80.0

Derivatives of *p*-Bromophenol.

γ -Hydroxypropyl-*p*-bromophenyl Ether, Br.C₆H₄.O.CH₂.CH₂.CH₂.OH.
—To obtain this substance, sodium *p*-bromophenolate was treated with trimethylene chlorohydrin in the manner given above for the corresponding *o*-tolyl ether. The product is a colorless liquid boiling at 206° at 48 mm. Yield, 75%, n_D^{22} , 1.563, d_{20} , 1.442.

Subs., 0.1930 AgBr, 0.1560
Calc. for C₉H₁₁O₂Br. Br, 34.6 Found. 34.4.



was dehydrated by heating with zinc chloride, and the product was purified by the method given. It is a water clear liquid with a pleasant odor, and is obtained in 7 to 10% yields. Phosphorus pentoxide would probably be a more satisfactory dehydrating agent than the one used. B. p. 143–144° at 18 mm., n_D^{22} , 1.580, d_{20} , 1.465.

Subs., 0.2124 AgBr, 0.1902.
Calc. for C₉H₇OBr Br, 37.6 Found. 38.0

β -Bromo-ethyl-*p*-bromophenyl Ether, Br.C₆H₄.O.CH₂.CH₂.Br.—For the synthesis of this compound, the directions given for the analogous cresol derivative were followed. The yield was about 25%. It boils at 165° at 16 mm. and changes on standing to a white solid melting at 55–56°.

Subs., 0.1743. AgBr, 0.2336.
Calc. for C₈H₇OBr₂ Br, 57.2. Found: 57.5.

4-Bromocoumarane.—When the ether just described was heated with $\frac{1}{10}$ its weight of fused zinc chloride, the temperature rose to 245° and hydrogen bromide fumes were given off. The thermometer reading gradually dropped to 200°. After taking up in ether and washing with

alkali and water in the usual way, the product was obtained as a colorless liquid with a pleasant odor boiling at 135° at 20 mm.; n_D^{22} , 1.555; d_{20} , 1.436.

Subs., 0.2156 AgBr, 0.2047

Calc. for C_8H_7OBr Br, 40.2 Found 40.5

β -Hydroxyethyl-*p*-bromophenyl Ether, $Br C_6H_4 O.CH_2.CH_2OH$.—This ether was prepared from ethylene chlorohydrin and *p*-bromophenol following the procedure already given. The substance distilled as a water clear liquid at 184° at 20 mm. On standing it solidified and melted at $49-50^{\circ}$. The yield was about 40%. On treatment with phosphorus pentoxide it dehydrated to give the 4-bromocoumarane described above.

Subs., 0.3000 AgBr, 0.2552

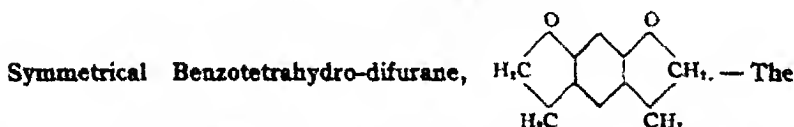
Calc. for $C_8H_7O_2Br$ Br, 36.8 Found 36.5

Derivatives of Resorcinol.

Di- β -hydroxyethyl-*m*-phenylene Ether, $C_6H_4(OCH_2CH_2OH)_2$.^{1,2}—For the preparation of this compound, sodium was dissolved in absolute alcohol, and resorcinol and ethylene chlorohydrin added in equivalent quantities. After refluxing, the mixture was fractionally distilled without aqueous dilution since the product is soluble in water. It was obtained from $230-234^{\circ}$ at 30 mm. as a viscous liquid which slowly solidified on standing. After washing with alcohol it was pure white and melted at 81° . It is soluble in alcohol and methylethyl ketone but insoluble in ether, benzene or ligroin. Yield, 40%.

Subs., 0.2000 CO_2 , 259.7 cc (24.3° , 749.9 mm)

Calc. for $C_{12}H_{14}O_4$ C, 60.6 Found 60.9



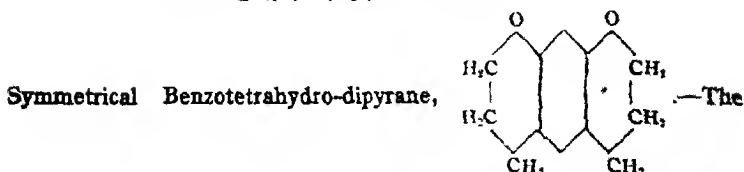
ether just described was dehydrated in methyl ethyl ketone solution by the action of phosphorus pentoxide according to the usual procedure. After most of the methyl ethyl ketone was distilled off water was added and the product extracted with ether. After washing and drying the cyclic ether was obtained as a disagreeably smelling, colorless liquid, boiling at $110-113^{\circ}$ at 148 mm., n_D^{22} , 1.448; d_{20} , 0.861.

Subs., 0.2415; CO_2 , 380.8 cc (24.5° , 734.5 mm)

Calc. for $C_{12}H_{12}O_2$ C, 74.0 Found 72.7

Di- γ -hydroxypropyl-*m*-phenylene Ether, $C_6H_4(OCH_2CH_2CH_2OH)_2$.^{1,2}—Resorcinol was added to sodium alcoholate and then treated with trimethylene chlorohydrin, equivalent quantities of each being used. After refluxing for several hours, the sodium chloride was filtered off and the mixture fractionated. The product is a pale yellow, viscous liquid. B. p., $246-248^{\circ}$, at 20 mm.; n_D^{24} , 1.529; d_{20} , 1.145.

Subs., 0.2747 CO_2 , 386.8 cc (30.3°, 738.8 mm)
Calc. for $\text{C}_{25}\text{H}_{18}\text{O}_4$: C, 63.7 Found 63.2



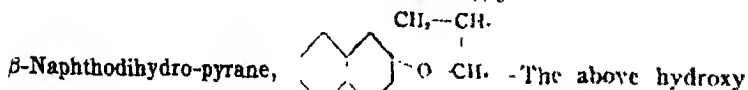
ether just prepared was treated with phosphorus pentoxide in methyl ethyl ketone solution. After heating for some time, the most of the ketone was distilled off the residue taken up in ether, washed with alkali and water, dried and distilled B. p., 97°, at 75 mm. Yield 15%; n_D^{20} , 1.448.

Subs., 0.1012 CO_2 , 16.1 cc (28.6°, 743.4 mm)
Calc. for $\text{C}_{17}\text{H}_{14}\text{O}_2$: C, 75.7 Found 75.3

Derivatives of β -Naphthol.¹

γ -Hydroxypropyl- β -naphthyl Ether, $\text{C}_{10}\text{H}_7\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$ —This was prepared in 25% yields by the usual method, and is a white solid which may be crystallized from benzene M. p., 99-99.5°

Subs., 0.3000 CO_2 , 522.3 cc (32.3°, 742.9 mm)
Calc. for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 77.2 Found 77.5

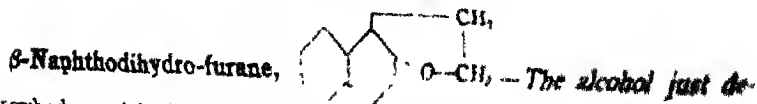


ether was dehydrated by phosphorus pentoxide in toluene in the usual way, and gave a viscous liquid which solidified on standing. After crystallization from alcohol, a white solid melting at 41-42° was obtained in 33% yield

Subs., 0.3000 CO_2 , 520.1 cc (32.6°, 742.5 mm)
Calc. for $\text{C}_{12}\text{H}_{10}\text{O}$: C, 84.7 Found 84.4

β -Hydroxyethyl- β -naphthyl Ether, $\text{C}_{10}\text{H}_7\text{OCH}_2\text{CH}_2\text{OH}$. —By the usual method, this compound was obtained as an impure solid which was purified with considerable difficulty. From 50% alcohol it separated as an amorphous compound, but from benzene it crystallized, and melted at 76-77°.

Subs., 0.3000 CO_2 , 520.5 cc (32.8°, 742.9 mm)
Calc. for $\text{C}_{11}\text{H}_{12}\text{O}_2$: C, 76.6 Found 76.9



scribed was dehydrated in benzene solution according to the usual method. The final product was a viscous dark oil boiling at 185° at 10 mm. and

¹ Assistance in experimental work was given by J. H. Brecht.

tending to decompose during distillation. The yields were low and the material not entirely pure; n_D^{25} , 1.482; d_{20} , 1.0066.

Subs., 0.2319 CO₂, 451.2 cc (32.5°, 742.5 mm)

Calc. for C₁₂H₁₀O·C, 84.8. Found 86.2

β -Bromo-ethyl- β -naphthyl Ether, C₁₆H₁₃O·CH₂CH₂Br.—Sodium naphthylate in absolute alcohol was treated with twice the theoretical amount of ethylene bromide. After refluxing, the alcohol and the excess ethylene bromide were distilled off and the desired product crystallized from alcohol. Melting point 91.5–92.5°. Yield 30%. Attempts to prepare β -naphthodihydro-furane from this by treatment with zinc chloride gave only carbonization and tars.

Subs., 0.3000 AgBr, 0.2221

Calc. for C₁₆H₁₃OBr Br, 31.87. Found 31.51.

Summary.

1. Cyclic ethers condensed to a benzene nucleus are easily prepared by dehydrating the appropriate hydroxy-alkyl-aryl ethers.

2. Zinc chloride or phosphorus pentoxide may be used for this, but the latter in general is the more satisfactory.

3. The following compounds were prepared:

	B. p. Degrees	M. p. Degrees	d	n
γ -Hydroxypropyl- <i>o</i> -tolyl ether	174–6 (42 mm)		1.053 (29°)	1.523
γ -Bromopropyl- <i>o</i> -tolyl ether	154–6 (20 mm)		1.299 (29°)	1.535
8-Methylchromane	114–6 (30 mm)		1.039 (29°)	1.542
β -Hydroxyethyl- <i>o</i> -tolyl ether	143–5 (20 mm)		1.079 (29°)	1.528
β -Bromo-ethyl- <i>o</i> -tolyl ether	133–4 (20 mm)		1.360 (29°)	1.544
6-Methylcoumarane	119–20 (65 mm)		1.000 (29°)	1.527
Hydroxypropyl- β -bromophenyl ether	206 (48 mm)		1.442 (24°)	1.563
6-Bromochromane	143–4 (18 mm)		1.465 (25°)	1.580
β -Bromo-ethyl- β -bromophenyl ether	165 (16 mm)	56		
4-Bromocoumarane	133 (20 mm)		1.436 (22°)	1.555
β -Hydroxyethyl- β -bromophenyl ether	184 (20 mm)	50		...
Di- β -hydroxyethyl- <i>m</i> -phenylene ether	230–4 (30 mm)	81		...
Symmetrical benzotetrahydrodifurane	110–3 (145 mm)		0.861 (25°)	1.448
Di- γ -hydroxypropyl- <i>m</i> -phenylene ether	246–8 (20 mm)		1.145 (31°)	1.529
γ -Hydroxypropyl- β -naphthyl ether		99.5		...
β -Naphthodihydro-pyran		47–2		...
β -Hydroxyethyl- β -naphthyl ether	185 (10 mm)		1.007 (30°)	1.482
β -Bromo-ethyl- β -naphthyl ether		92		...
Symmetrical benzotetrahydro-dipyran	97 (75 mm.)			1.448

UENAGA, ILL.

[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY,
U S DEPARTMENT OF AGRICULTURE]

OKRA SEED OIL.¹

BY GEORGE S. JAMIESON AND WALTER F. BAUGHMAN

Received November 12, 1919

The object of this investigation was to prepare several samples of okra seed oil and determine the so-called constants for each sample, in addition to making a study of the chemical composition of the oil.

Several lots of the seed of okra (*Abelmoschus esculentus*, Malvaceae) were received at various times from E. A. McIlhenny, of Avery Island, La., through David Fairchild of the Department of Foreign Seed and Plant Introduction of the Bureau of Plant Industry. The first samples of okra seed were received about two years ago, and H. S. Bailey obtained the cold pressed oil from these seeds by means of an expeller. Shortly afterwards, H. S. Bailey and J. M. Johnson made a preliminary examination of these samples of oil, and their results, which have recently been confirmed by us, have been incorporated in this paper.

Last January another 150-pound sample of the Avery Island okra seed was sent to this laboratory. The seed were pressed in the expeller, with the result that 12 pounds of virgin okra seed oil were obtained. The oil had a pleasing, greenish yellow color, and a slight but distinct fragrant odor. This seed was found to contain 15.60% of oil and 5.63% of moisture. The press cake contained 5.88% of oil.

It is interesting to observe that okra seed oil, as well as oils obtained from other members of the Malvaceae, has been found to give the Halphen color test.²

TABLE I

Sample number	1	2	3.	4
Iodine number (Hanus)	93.2	100.3	95.5	95.2
Saponification number	195.5	195.6	195.6	195.2
Polenske number				0.23
Reichert-Meißl number.			..	0.26
Acetyl value	23.9	16.2	11.5	21.4
Acid value		0.66	0.34	1.43
d_{25}^{25}	0.9187	0.9182	0.9160	0.9173
Refractive index at 25°	1.4692	1.4693	1.4695	1.4702
Unsaponifiable matter, %				0.37
Soluble acids, %		0.12	0.09	0.14
Insoluble acids, %		95.90	96.27	96.20
Unsaturated acids, %				67.33
Saturated acids, %				29.22

Sample 4 was the oil obtained from the 150-pound sample of seed mentioned above

¹ Published by permission of the Secretary of Agriculture

² S. L. Ivanov and N. P. Kokotkina, *Sobshch. Russk. Khim. Obshch.*, [2] 1913, No. 7, 3 to 24

When the Renard test for arachidic acid was applied to a 20 g. portion of the oil, 2.2 g. of fatty acids were obtained, which were found to melt at about 58° . After two recrystallizations of these fatty acids from alcohol, the melting point was raised only a degree; this indicated, as in the case of tomato seed oil,¹ that the Renard test was not applicable to this oil. The preceding table contains the results of the analyses of 4 okra seed oils.

The table given below contains the analysis and other data obtained from the insoluble acids, saturated and unsaturated acids, of Sample 4.

	Insoluble acids	Saturated acids	Unsaturated acids.
Iodine number (Hanus) ..	97.3	5.7	137.9
Saponification number...	210.6	215.6	199.2
Mol. wt.....	266.4	260.1	281.6
Acetyl value.			25.4
M. p.	$40-41^{\circ}$		
Titer	38.5°		

The unsaturated acids had a beautiful green color.

In order to identify and to determine the approximate amount of unsaturated fatty acids, a portion of 30 g. of okra seed oil was taken and these acids were separated by the well-known lead-salt ether process. Precautions were taken to prevent the oxidation of the unsaturated liquid acids by evaporating the ether solutions of these acid in an atmosphere of dry carbon dioxide. For the identification and separation of the unsaturated acids the bromine method of Eibner and Muggenthaler² was employed. A 10 g. sample of the acids, dissolved in 90 cc. of absolute ether, was cooled to -10° , and 5 g. of bromine was slowly added, drop by drop. During the addition of the bromine, the temperature was not allowed to rise above -5° . After the addition of the bromine, the contents of the bromination flask were allowed to stand at -5° for 2 hours. The small amount of crystalline material which had separated was filtered in a weighed Gooch crucible, washed with cooled absolute ether, dried at 100° , and weighed. The crystals weighed 0.3727 g.; they melted at 114° , which showed that the compound was the tetrabromide of linolic acid, and that the unsaturated acids which form insoluble octa- and hexabromides were absent. The excess of bromine was removed from the filtrate in the usual manner with sodium thiosulfate, and after the ether was removed by distillation, the bromides were dissolved in hot petroleum ether. After cooling, the solution was allowed to stand for several hours, and then the separated tetrabromide was filtered and weighed. This crop of crystals weighed 4.9839 g. The filtrate was concentrated to less than half of its original volume, and again cooled and allowed to stand as before. After filtering this crop of tetrabromide crystals, which weighed 0.5296 g., the filtrate was evaporated to a volume of 25 cc., and allowed

¹ *J. Ind. Eng. Chem.*, 11, 850 (1919)

to stand in the ice box overnight, and no more crystals separated. Each crop of crystals was found to melt at 114° , the melting point for tetrabromo-linolic acid. As it was impossible to get any more of the tetrabromide to separate, all of the petroleum ether was removed, and the residue of tetrabromide linolic acid and dibromoleic acid was weighed. The bromine content was determined by boiling portions of the residue with conc. nitric acid and solid silver nitrate. Oleic dibromide contains 36.18% of bromine, and linolic tetrabromide contains 53.33%. Therefore, knowing the bromine content of the residue, it is possible to calculate the proportions of dibromide and tetrabromide present. The data obtained from the examination of the unsaturated acids are given in the following table:

	C
Sample of unsaturated acids	10 0000
Linolic tetrabromide crystallized	5 8862
Residue (di- and tetrabromide)	12 4153
Dibromide in residue 80.47% or	9 9900
Tetrabromide in residue 19.53% or	2 4247
Total tetrabromide	8 3109
Linolic acid = tetrabromide	3 8784 or 38.78%
Oleic acid = dibromide	6 3741 or 63.74%

The percentages of linolic and oleic acids in the unsaturated acids were calculated into the percentages of the glycerides in the original oil as follows:

	Found %	Calc. to basis of 100% %	In original oil %	Glycerides in oil %
Oleic acid	63.74	62.17	41.86	43.74
Linolic acid.	38.76	37.83	25.47	26.62
Total...	102.52	100.00	67.33	70.36

Examination of Saturated Acids.

From 242 g. of okra seed oil, 70.7 g. of saturated acids were obtained. The methyl esters of these acids were prepared in the same manner as the esters of the saturated acids of tomato seed oil,¹ and distilled under diminished pressure. The following table contains the data of the distillation of 64.9 g. of the methyl esters

Fractions	Temperature $^{\circ}$ F.	Pressure mm.	Wt. of fractions (g.)
1	170-173.5	5.0	24.7
2	170-174	5.0	22.7
3	174-175	5.0	11.2
	178-186	5.0	
	187-192	5.0	

The fractions in turn, as their boiling points were reached, were returned to the distilling bulb and refractionated in order to get a better separation of the esters. The following table contains the results of the analyses of 7 fractions, obtained by the redistillation of the fractions.

Frac-tions	Wt of frac-tions G	Iodine num-ber	Saponi-fica-tion value	Mean mol wt	Palmitic acid		Stearic acid		Arachidic acid		Unsaturated acids	
					G	%	G	%	G	%	G	%
1.	23 2	.	.	.	22 00	94 82						
2	21 8	3 1	206 4	271 8	19 46	89 46	0 72	3 32			0 49	2 25
3	10 8	5 9	204 3	274 6	8 63	79 93	1 15	10 68			0 46	4 28
4	2 3	12 8	193 9	289 3	0 48	20 98	1 49	64 93			0 21	9 28
5	1 0	14 9	190 8	294 1	0 14	14 06	0 70	70 37			0 10	10 00
6	0 8	16 3					0 62	77 50	0 051	6 38	0 09	11 80
7	0 63						0 47	75 50	0 051	8 10	0 08	12 00

The distillation was continued until the small residue remaining in the distilling bulb charred. An attempt was made to isolate and identify the acids in this residue, but on account of the small amount of ester present it was found impossible.

It should be observed that the saponification values of Fractions 6 and 7 were not determined on account of the smallness of these fractions. The free fatty acids were obtained from these fractions by saponification, and precipitation with hydrochloric acid in the usual manner, and the arachidic acid was separated from the stearic acid by fractional crystallization from 95% alcohol. The arachidic acid obtained from Fractions 6 and 7, which was found to melt at 76°, was analyzed by Mr. Charles E. F. Gersdorff with the following results

Subs. (Fraction 6), 0.0507 CO_2 , 0.1428, H_2O , 0.0604

Calc for $\text{C}_{18}\text{H}_{34}\text{O}_2$ C, 76.85, H, 72.91 Found C, 76.82, H, 13.24

Subs. (Fraction 7), 0.0509 CO_2 , 0.1435, H_2O , 0.0609 Found C, 76.89, H, 13.29.

Both of the analyses as well as the melting points proved that it was arachidic acid.

The free acids recovered from Fraction 5 were repeatedly crystallized from 95% alcohol until the constant melting point of 67 to 68° was obtained, then this acid was analyzed by Mr. Gersdorff with the following results:

Subs., 0.1058 CO_2 , 0.2946, H_2O , 0.1214

Calc for $\text{C}_{18}\text{H}_{34}\text{O}_2$ C, 75.98, H, 12.76 Found C, 75.94, H, 12.75

The analysis showed that the compound was stearic acid.

Acids	Wt (%)	%	Acids in oil %	Glycerides in oil %
Palmitic.....	50.71	88.36	25.82	27.23
Stearic.....	5.15	8.98	2.62	2.73
Arachidic.....	0.10	0.17	0.05	0.05
Unsaturated.....	1.43	2.49	0.73	...

The percentages of the saturated acids and their glycerides in the original oil have been calculated from the analytical data with the preceding results.

Summary.

The chemical characteristics of 4 samples of cold pressed okra seed oil have been determined. These oils vary slightly in composition. An exhaustive study has been made on the composition of the recently expressed oil No. 4, the results of which are given in the following table:

Glycerides of	%
Palmitic acid	27.23
Stearic acid	2.75
Arachidic acid	0.05
Oleic acid	43.74
Linolic acid	26.62
Unsap.ifiable matter	0.37

WASHINGTON, D. C.

NEW BOOK.

The Condensed Chemical Dictionary. Compiled and edited by the Editorial Staff of the Chemical Engineering Catalog, of which F. M. TURNER, JR., is Technical Editor and D. D. BEROLZHEIMER, W. P. CUTTER and JOHN HELFRICH are Assistant Editors. The Chemical Catalog Company, Inc., 1 Madison Ave., New York, 1919. 525 pp. \$5.00 net.

The title page of this useful book describes it as being "a reference volume for all requiring quick access to a large amount of essential data regarding chemicals and other substances used in manufacturing and laboratory work." While it is intended primarily to supply in readily available form the outstanding facts regarding such substances to people not chemically trained who are being brought into contact with the chemical industries in greater numbers with the growing importance of these industries, the book will serve as a great time-saver for the chemist who keeps it at hand.

Many substances of scientific interest but not important commercially have been omitted. Therein lies the chief significance of the word "condensed" in the title for, although it is stated that no attempt has been made to produce an exhaustive work, the field of commercially important chemical substances, excepting dyes, appears to have been pretty thoroughly covered.

Under the various headings information is given, with such variations as the nature of the substances may require, on derivation, habitat, color and other properties (restricted to those properties likely to be of commercial importance), constants, method of purification, grades, containers, uses, impurities, fire hazard, railroad shipping regulations and occasionally other information. Under "Derivation" a general idea of the method of

manufacture is given in the case of substances which are not natural products.

At the back of the book are to be found tables of (1) atomic weights (the title of this strictly atomic weight table is misleading; it reads "Combining (Atomic) Weights"), (2) domestic weights and measures, (3) metric equivalents, (4) equivalent temperature readings for Fahrenheit and Centigrade scales, and (5) specific gravity equivalents for degrees Baumé, and, in addition, a list of definitions of units and information regarding the transportation by freight of dangerous articles other than explosives.

The thorough manner in which the dictionary is cross-indexed is a most valuable feature. It is a well-known and unfortunate fact that a great many chemical substances have several used names. Cross-references direct the user of the dictionary to the name which has been given the preference. By this means the dictionary will do good service in helping users to ascertain the meaning of more or less obscure names. It seems as though considerable space might have been saved without loss by the use of an occasional general cross-index entry to replace a series of like ones. For example, a single brief note under the heading "Oils" explaining how oils have been handled might have replaced over 5 pages of cross-index entries starting with the word "Oil."

In a dictionary prepared chiefly for those interested in the commercial side of chemistry it is perhaps to be expected that the nomenclature will be influenced by commercial usage, which does not always agree with the usage best from theoretical considerations. One gets the impression in looking through the Condensed Chemical Dictionary that the compilers have in general tried to use for a compound the name to be preferred from a scientific standpoint when a commercial name which is different is not too predominately in use. This seems to be a reasonable attitude. It is hard to pass by, however, without expressing a hope for at least one change, namely, that some day in the dictionary, the trade and more generally elsewhere the name "hydroxy" instead of "oxy" will be adopted for the OH group in compounds. And it goes against the grain a bit to see thiocyanates (-CNS) called "sulfocyanides." The new official names for certain licensed synthetic pharmaceuticals now manufactured in this country, such as "barbital," have not been given preference over the names of the German products ("veronal" in the example just given). The spelling follows the rules set forth in "Directions for Assistant Editors and Abstractors" of Chemical Abstracts.

No abbreviations have been used. To many this will no doubt appeal as being a satisfying departure from the usual practice in dictionaries; to others it will probably seem that a good deal of space should have been saved by the use of some of the more common abbreviations at least

as sp. gr. for specific gravity. The spacing between the entries and at the bottom of the page is such as to leave a little room for memoranda.

An interesting feature of the dictionary is the designation by marking with an asterisk of all of those substances now made in America. It is pleasant to note so many asterisks

E J. CRANE.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE KANSAS STATE AGRICULTURAL COLLEGE.]

A STUDY OF THE DETERMINATION OF AMINO ACIDS BY MEANS OF THE HYDROGEN ELECTRODE.

By E. L. TAGUE

Received April 29, 1919

Some time ago the writer began a series of investigations on the conditions for the activity of proteoclastic enzymes of wheat and flour.¹ The extent of protein hydrolysis in the auto-digestion experiments was determined by means of the formol titration method of Sørensen. After this had been used for some time an attempt was made to substitute electrometric titration for it. The results obtained were so encouraging that further work was deemed advisable. Before much headway could be made in the study of protein hydrolysis of flour, however, it was necessary to know the behavior of the different degradation products of protein hydrolysis upon the hydrogen electrode. A few of the simpler amino acids were first investigated from this point of view, namely glycocoll, a monoamino monocarboxylic acid; phenylalanin, a monoamino monocarboxylic acid containing the benzene ring; lysin, a diamino monocarboxylic acid; glutamic acid, a monoamino dicarboxylic acid; and tyrosin, a monoamino monocarboxylic acid containing an hydroxyl group in the benzene ring.

Several investigators have determined the hydrogen

of aqueous solutions containing glycocoll and sodium hydroxide, and glycocoll and hydrochloric acid in different proportions. These mixtures are used as standards in the colorimetric determination of the hydrogen ion. As far as the writer knows, however, none of these investigators has differentiated between the excess alkali necessary to overcome titration and the amount of alkali necessary to neutralize the solute. Strictly speaking, neutralization consists in bringing the concentration of the hydrogen or hydroxyl ions to a concentration of 1×10^{-7} gram ions per liter, or P_H 7.00. Certain substances, however, such as amino acids, require the presence of an excess of hydroxyl ions before they will show their maximum acid characteristics, or an excess of hydrogen ions before they will show their maximum basic nature. Consequently in titrating an amino acid with a base it is necessary to have the concentration of the hydroxyl ion greater than 1×10^{-7} in order to neutralize the acid quantitatively. Even with the formol titration method of Sørensen, where the basic nature of the amino acid is first destroyed by formaldehyde, it is necessary to have an excess of hydroxyl ions. In such cases a certain proportion of the added hydroxyl ions are used up in bringing the solvent itself to the hydroxyl ion concentration required for complete neutralization of the solute. It should be possible then to titrate aqueous solutions of amino acids without the previous addition of formaldehyde provided proper corrections are made for this factor. The hydrogen electrode furnishes a means for the accurate determination of this factor.

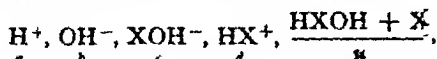
The ionization equilibria of the amino acids, since they are amphoteric electrolytes, would be represented by the following equations (1) by hydration: $\text{NH}_2\text{R.COOH} + \text{H}_2\text{O} \rightleftharpoons \text{OH.NH}_2\text{R.COOH}$; (2) and then (a) as an acid, $\text{OH.NH}_2\text{R.COOH} \rightleftharpoons \text{H}^+ + \text{OH.NH}_2\text{R.COO}^-$; (b) as a base, $\text{OH.NH}_2\text{R.COOH} \rightleftharpoons \text{N}^+\text{H}_3\text{R.COOH} + \text{OH}^-$, (c) an inner salt, $\text{OH.NH}_2\text{R.COOH} \rightleftharpoons \text{N}^+\text{H}_3\text{R.COO}^- + \text{H}^+ + \text{OH}^-$, (d) $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$.

All these equilibria would exist side by side. The relative values of each would depend on the magnitude of the ionization constants of the amino acid as (1) an acid, (k_a); (2) a base (k_b); (3) an inner salt (k_c). The ionization equilibria of all the amino acids studied in this paper would reduce finally to the above equations, although in the case of both the dicarboxylic acids and the diamino acids there would be intermediate equilibria, depending on the primary and secondary ionizations as an acid, or as a base, respectively.

Owing to the amphoteric character of the amino acids, their degree of ionization is comparatively small. For the most part their acid characteristics are stronger than their basic. Consequently their aqueous solutions react slightly acid. When the constants k_a and k_b of an amino acid are equal, the substance is neutral, i. e., the concentration of the hydrogen

and hydroxyl ions are the same as in pure water. Notwithstanding this neutrality, the solution of the acid would still be an electrolyte because of its ionization as an inner salt, and it would still be capable of acting as a base toward acids and an acid toward bases. In all neutralization reactions, then, the inner salt would tend to hydrate and subsequently as a base as the hydrogen ion concentration of the solution approached the ionization constant of the acid as a base.

According to Walker,¹ if the concentrations of the different substances taking part in the above equilibrium are represented as follows:



then the equilibrium of the hydrogen ion is represented by the equation

$$a^2 = \frac{K + k_a u}{1 + k_b u}$$

where a is the concentration of the hydrogen ion, K the ionization constant of the water, k_a the ionization constant of the ampholyte as an acid, k_b the constant of the ampholyte as a base, and u the concentration of the undissociated molecules.

The addition of sodium hydroxide to an aqueous solution of an amphoteric electrolyte would decrease a . This decrease in a would have 2 separate effects on the right-hand side of the above equation. (1) u would decrease; (2) k_b of the ampholyte would decrease, since an increase in the hydroxyl ion concentration of the solution would cause a decrease in the basic characteristics of the ampholyte. In other words, the result would be the same as though a series of amphoteric acids with decreasing k_b were dissolved separately in a given volume of water and the above equilibrium formula applied. As the hydrogen ion concentration of the solution approached the value k_b , the value of the magnitude, $\frac{k_b u}{K}$ would

decrease and the expression $a^2 = \frac{K + k_a u}{1 + k_b u}$ would become finally $a^2 =$

$\frac{K + k_a u}{1 + k_b u}$, which is the expression for a simple acid with the same acid constant k_a . The further addition of sodium hydroxide would cause a further decrease in a and thus a corresponding decrease in u . Consequently the expression $a^2 = \frac{K + k_a u}{1 + k_b u}$ would tend to become $a^2 = K$, i. e., the concentration of the hydrogen and hydroxyl ions as far as the inner salt is concerned would be the same as the pure water. This means that from this point on the solute has no further influence on the equilibrium. Therefore, the amount of hydroxyl ion necessary to bring a solution of an amino acid to equilibrium at any point of less hydrogen ion concentration than the k_b of that acid would be:

$$\text{OH}_X^- = \text{OH}^-_{\text{neutralization}} + \text{OH}^-_{\text{hydration}}$$

where $\text{OH}^-_{\text{neutralization}}$ is the amount necessary to neutralize the solute to that point, and $\text{OH}^-_{\text{hydration}}$ the amount necessary to overcome hydration at the same point. At all points of greater hydrogen ion concentration than k_b , the amount of base necessary to add would be less than OH_X^- because of the ionization of the inner salt as a base. The ratio between $\text{OH}^-_{\text{neutralization}}$ and $\text{OH}^-_{\text{hydration}}$ would be given by the formula of Walker above mentioned. As soon as the concentration of the hydroxyl ion is sufficient to reduce the concentration of the hydrogen and hydroxyl ions, resulting from the dissociation of the inner salt, to the same value as that of the same ions in pure water, the solute has been quantitatively neutralized, and $\text{OH}^-_{\text{neutralization}}$ becomes a constant.

This investigation of the amino acids then resolves itself into a study of 3 factors: the behavior of (1) the solute plus solvent, (2) the solvent alone, (3) the solute alone. The values of the third can be calculated from those of the first and second.

If to a given volume of the amino acid solution, different portions of a standard alkali are added, and after each addition the P_H value is determined by the hydrogen electrode, a set of values are obtained which show the amount necessary to neutralize the solute and overcome hydration of the solvent plus solute to the same points. Again, if sufficient standard alkali is added to a like volume of the solvent alone so as to bring it to the same P_H values as those obtained with the original solution, care being taken to have the volumes the same at each point measured, respectively, another set of values are obtained which show the amount necessary to overcome the hydration of the solvent alone. Since the P_H values are the same in both cases, subtracting the cc of alkali necessary to bring the solvent itself to any P_H value, from those used in bringing the solvent plus solute to the same P_H values, will give a set of values which show the course of neutralization of the solute alone. In this way the behavior of the amino acid itself can be determined and its own course of neutralization observed.

Apparatus and Solutions Used.

The apparatus contains the following pieces: a Kohlrausch slide wire bridge; a Type B (No. 2500) Leeds and Northrup galvanometer; a Weston¹ millivoltmeter and multiplier; Edison storage cells; and the hydrogen and normal calomel electrodes made according to the directions of Hildebrand.¹

Hydrogen made by the electrolytic process was used, and, as a precaution against impurities, the gas was washed in a train of bottles contain-

¹ Joel H. Hildebrand, "Some Applications of the Hydrogen Electrode in Analysis, Research, and Teaching," *THIS JOURNAL*, 35, 847 (1913)

ing 2% permanganate solution, alkaline pyrogallie acid, and mercuric chloride. The electrodes as well as the tips of the burets were inserted through a rubber stopper which fitted the electrode vessel. In this way the solution was effectively protected from the carbon dioxide of the air. The electrode vessel was connected to a suitable shaking device run by a small electric motor. The calomel cell, electrode vessel, and connections were placed in a suitable bath and the temperature kept constant at 18°.

The water, distilled, using condensers of block tin, was collected and kept in old glass containers which had been used for this purpose for several years. Carbon dioxide free air was passed through this water until it was practically free from carbon dioxide, and gave a P_H value of 6.0 to 6.6. All solutions used in this experiment were made up from this water and carefully protected at all times from the carbon dioxide of the air.

Tenth molar solutions of the amino acids were used. The requisite amount of each acid was weighed out and dissolved in water, excepting tyrosin, which was dissolved in 30 cc. of 0.1 *N* hydrochloric acid, and the solutions made up to volume with water. It was desired to compare the results obtained here with those from the work on wheat and flour. Since 100 cc. was the volume used in that investigation, the same volume was adopted here.

The alkali used was 0.1 *N* sodium hydroxide solution. Two hundred g. of the c. p. salt was dissolved in 300 cc. of carbon dioxide free water. In alkali of this strength the carbonates are insoluble.¹ From this solution portions were pipetted off and used in making up the 0.1 *N* solution. The alkali was standardized against 0.1 *N* sulfuric acid, using phenolphthalein as indicator.

Procedure with the Hydrogen Electrode.

Influence of Solvent on Titration.—Since it was desired to differentiate between the solvent and the solute, the first question investigated was the behavior of water under the conditions of the experiment. The curve obtained experimentally by the addition of different portions of standard alkali to a given volume of water and the determination of the P_H value by the hydrogen electrode after each addition will show what influence the solvent has on investigations of this kind. This curve can be calculated also, and thus it serves as a check on the purity of the water used and on the accuracy of the method.

One hundred cc. of water was pipetted into the electrode vessel and hydrogen gas passed through until equilibrium was attained. This usually required 30 to 60 minutes. During the entire time the electrode vessel was shaken 50 to 60 times per minute. As soon as the potential remained

¹ Michaelis, Leonor, *Wasserstoffionen-Konzentration*, 1912, p. 177.

constant within one millivolt for 15 minutes, 0.1 cc. of 0.1 *N* alkali was added from a buret. The solution was allowed to come to equilibrium as before. The potential was noted and alkali run in again until 0.2 cc. had been added. The constant potential was determined again and noted. In this way definite portions of alkali, as noted in Table I, were added and after each addition the constant potential was determined and noted. This was continued until 50 cc. altogether had been added. Preliminary experiments showed that it was not necessary to go beyond this value in the present experiment.

In Table I will be found the data thus obtained, together with the theoretical values

The concentrations of the hydrogen ion were calculated by the following formula:

$$E = 0.0577 \times \log I/c + 0.283 \quad (1)$$

where *E* is the potential in volts at equilibrium; *C* the concentration of the hydrogen ion in gram ions per liter; 0.0577 the value of the constant *RT/F* at 18° as given by Nernst;¹ and 0.283 the potential difference between the normal potassium chloride electrode and the normal hydrogen electrode as zero.² If the ionization constant of water at 18° be taken as 0.64×10^{-14} as given by Nernst,³ then

$$OH^- = \frac{0.64 \times 10^{-14}}{H^+} \quad (2)$$

The theoretical values were calculated by the following formula:

$$OH = \frac{A \times N}{100 + A} \times I$$

where OH = concentration of OH⁻ ions in gram ions per liter; *A* = cc. of alkali added, *N* = normality of alkali; *I* = per cent of ionization.

For example, when 50 cc. of 0.1 *N* sodium hydroxide is added to 100 cc. of water, the formula becomes

$$OH = \frac{50 \times 0.1}{150} = 0.03333$$

At this concentration *I* = 93.5 (%), whence

$$OH = 0.03333 \times 93.5 = 3.12 \cdot 10^{-2}$$

The percents ionization were obtained from a graph constructed from the data given by Prideaux.⁴

¹ Nernst, *Z. Elektrochem.*, 12, 1 (1906); 9, 686 (1903), 10, 629 (1904); 11, 537 (1905).

² Wilsmore, *Z. physik. Chem.*, 35, 291-332 (1900); Ostwald and Wilsmore, *Ibid.*, 36, 91 (1901).

³ Nernst, *Z. physik. Chem.*, 14, 153 (1894).

⁴ Prideaux, "Theory and Use of Indicators," 1917, p. 28, New York.

TABLE I.
Addition of Standard Alkali to 100 cc. of Water.

Cc. 0.1 <i>M</i> NaOH.	Volt.	<i>P_H</i> .	Gram ions OH (determined)	Gram ions OH (calculated).	Ionization %
Equil.	0.656	6.462	$1.853 \cdot 10^{-3}$
0.1	0.868	10.136	$8.78 \cdot 10^{-4}$	$9.99 \cdot 10^{-3}$..
0.2	0.884	10.413	$1.67 \cdot 10^{-4}$	$1.98 \cdot 10^{-4}$	99.5
0.5	0.910	10.864	$4.70 \cdot 10^{-4}$	$4.92 \cdot 10^{-4}$	98.9
1.0	0.928	11.176	$9.62 \cdot 10^{-4}$	$9.71 \cdot 10^{-4}$	98.1
5.0	0.967	11.853	$4.57 \cdot 10^{-3}$	$4.54 \cdot 10^{-3}$	95.4
10.0	0.983	12.130	$8.64 \cdot 10^{-3}$	$8.64 \cdot 10^{-3}$	95.1
20.0	0.998	12.389	$1.57 \cdot 10^{-2}$	$1.58 \cdot 10^{-2}$	94.7
30.0	1.006	12.527	$2.17 \cdot 10^{-2}$	$2.17 \cdot 10^{-2}$	94.3
40.0	1.011	12.614	$2.63 \cdot 10^{-2}$	$2.68 \cdot 10^{-2}$	94.0
50.0	1.015	12.684	$3.09 \cdot 10^{-2}$	$3.12 \cdot 10^{-2}$	93.5

Titration of the Amino Acid Solution.—Twenty-five cc. of 0.1 *N* glycocoll solution and 75 cc. of water were pipetted into the electrode vessel and hydrogen gas passed through until equilibrium was attained. Then different portions of 0.1 *N* alkali were added from a buret, as indicated in Table II, and after each addition the equilibrium point was noted in exactly the same manner as in the preceding experiment. The addition of alkali was continued until the solution had a *P_H* value of about 12.5. Preliminary experiments had shown that all the amino acid was neutralized before this value was reached. When the values thus obtained were plotted, as in Fig. 2, a curve was obtained which shows the course of neutralization of the solute and the behavior of the solute plus the solvent under hydration. But since the curve of neutralization of the solute was desired, it became necessary to determine the blank.

Determining the Blank.—By the term "blank" is meant the cc. of alkali necessary to bring the solvent itself to the same *P_H* values as those obtained by the addition of definite portions of alkali to the solution of the amino acid. Since 100 cc. of the solution of the amino acid was used, 100 cc. of water was taken in determining this blank. To this 0.1 *N* alkali was added in such portions as were necessary to bring the blank to equilibrium at the same *P_H* values as those obtained in the solution of the amino acid. But since the solution of the amino acid always required more alkali to bring it to a certain *P_H* value than the same volume of water alone, sufficient water must be added at each *P_H* value to bring the blank to the same volume as that of the original. For example, 10 cc. of alkali produced a *P_H* value of 9.57 in the glycocoll solution. The total volume at this point was 110 cc. It required 0.1 cc. of alkali and 9.9 cc. of water to give the blank a *P_H* value of 9.57 and a total volume of 110 cc. The water was added to the electrode vessel from a second buret. In practice sufficient alkali was added to the blank to

bring it to equilibrium at approximately P_H 9.57, care being taken not to over run. From this a rough estimate of the amount of water to be added could be made. Somewhat less than the estimated amount was added and the solution brought to equilibrium again. This addition of water or alkali was repeated until the blank came to equilibrium at P_H 9.57 with a total volume of 110 cc. Subtracting the cc. of alkali necessary to bring the blank to the value P_H 9.57 from the cc. which produced the same value in the original solution, gave the cc. of alkali necessary to neutralize the amino acid to the same point. Thus of the entire 10 cc. of alkali added to the glycocoll solution, 0.1 was apportioned to the solvent and 9.9 cc. to the solute. If the blank is determined in this way for all the P_H values obtained in the original solution and the cc. thus obtained subtracted from the cc. obtained in the titration of the glycocoll, a set of values is obtained which represents the course of neutralization of the acid itself. As soon as all of the acid is neutralized this value becomes constant and the curve from that point on runs parallel to the P_H axis. Thus the method becomes a quantitative one. The results are set forth in Table II. Fig. 1 shows this method of differentiating between the solvent and solute.

TABLE II
Titration of the Solution of Glycocoll

Volts.	P_H	Cc N/10 NaOH added to gly- cocoll solution	Cc N/10 NaOH for blank	Cc N/10 NaOH used in neutralising amino acid alone
0 700	7 22	Equi		
0 712	7 44	0 1		..
0 749	8 08	0 5		0 1
0 767	8 38	1 0		0.5
0 797	8 90	3 0		1.0
0 812	9 16	5 0		3.0
0 835	9 57	10 0	..	3.0
0 855	9 91	15 0	0 1	9 9
0 877	10 30	20 0	0 2	14 8
0 914	10 93	25 0	0 3	19 7
0 940	11 38	28 0	1 3	23.7
0 951	11.58	30 0	3 2	24 8
0 9785	12 05	40 0	5 0	25.0
0 987	12 20	50 0	15 1	24 9
1 008	12 56	100 0	25 0	25.0
			75 0	25.0

Phenylalanin, tyrosin, lysin and glutamic acid were investigated in the same way. The data is set forth in Table III. In the column headed "Corrected, cc." are found the cc. of alkali necessary to neutralize the amino acid alone to the corresponding P_H value. Fig. 2 shows the curve of neutralization for each amine acid.

TABLE III.
Titration of the Amino Acids.

NaOH added Cc	NaOH blank Cc.	Corrected Cc	Volt	P _H
Phenylalanin.				
Equi.	0.518	4.07
0.1	.	0.1	0.527	4.23
0.2	..	0.2	0.531	4.29
0.5	..	0.5	0.546	4.56
1.0		1.0	0.573	5.02
5.0	..	5.0	0.769	8.42
10.0	..	10.0	0.800	8.95
15.0	..	15.0	0.822	4.34
20.0	0.2	19.8	0.845	9.74
25.0	0.5	24.5	0.891	10.53
28.0	2.9	25.1	0.938	11.35
30.0	5.0	25.0	0.949	11.58
40.0	15.0	25.0	0.976	12.01
50.0	25.0	25.0	0.987	12.20
Tyrosin.				
Equi.	.	..	0.437	2.67
1.0	..	1.0	0.497	3.70
5.0	.	5.0	0.724	7.64
10.0	..	10.0	0.802	9.00
20.0	..	20.0	0.846	9.76
30.0	0.2	29.8	0.868	10.14
40.0	0.5	39.5	0.891	10.53
50.0	2.6	47.4	0.931	11.23
60.0	11.5	48.5	0.966	11.84
70.0	20.4	49.6	0.979	12.06
80.0	29.7	50.3	0.987	12.20
90.0	39.3	50.7	0.992	12.29
100.0	50.0	50.0	0.997	12.37
130.0	79.6	50.4	1.005	12.51
Lysin-Dihydrochloride.				
Equi.			0.395	1.94
0.3		0.3	0.396	1.96
1.5	.	1.5	0.397	1.97
10.0	..	10.0	0.413	2.25
15.0		15.0	0.425	2.46
20.0	..	20.0	0.447	2.84
25.0	..	25.0	0.706	7.33
30.0	..	30.0	0.835	9.57
45.0	..	45.0	0.845	9.74
60.0	0.9	59.1	0.900	10.73
75.0	5.1	69.9	0.944	11.45
85.0	12.5	72.5	0.965	11.82
100.0	25.2	74.8	0.980	12.08
120.0	45.1	74.9	0.9925	12.38
150.0	75.0	75.0	1.0013	12.46

TABLE III (continued)

NaOH added Cc	NaOH blank. Cc	Corrected Cc	Volt	P_H
Glutamic Acid				
Equi			0.471	3.26
0.2		0.2	0.472	3.27
1.0		1.0	0.475	3.33
5.0		5.0	0.498	3.73
10.0		10.0	0.517	4.05
20.0		20.0	0.563	4.85
26.0		26.0	0.773	8.49
30.0		30.0	0.814	9.20
40.0		39.9	0.856	9.93
50.0	0.1	49.9	0.906	10.79
56.0	6.8	49.2	0.954	11.63
60.0	9.9	50.1	0.961	11.75
80.0	30.0	50.0	0.987	12.20
100.0	50.0	50.0	0.9967	12.37

Discussion of Results.

Differentiation between Solvent and Solute. The colorimetric method is laborious, and the errors due to the presence of salts, proteins, and other substances render the results in some cases well-nigh worthless. The hydrogen electrode makes possible an exact differentiation between an amount of alkali or acid to be apportioned to the solvent and solute, respectively, at any P_H value. The results shown in Table II

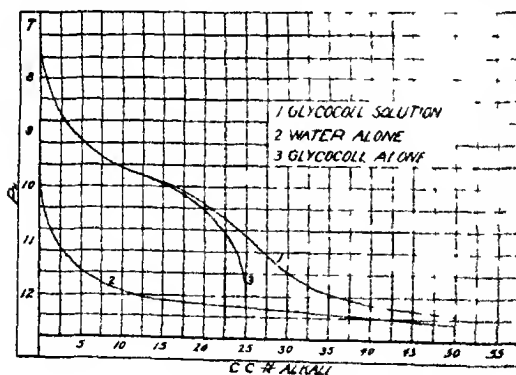


Fig. 1.—Method of differentiating between the solvent and the solute

and graphically in Fig. 1 illustrate this method of differentiation. Since at each P_H value the concentration of the OH^- ion both in the blank and in the solution of the amino acid are the same and the volume of the original solution and the blank are equal, there would be no difference in ionization in the observed results for the blank and for the solution of amino acid. In case the blank is calculated, however, a correction must be made for ionization. It will be noted in Fig. 1 that the further addition of alkali beyond the P_H value, 11.58, merely increases the hydroxyl ion concentration of the solvent alone. From this point on the curve for the solute runs parallel to the P_H axis. At this point the solute has been

quantitatively neutralized. The ionization of sodium glycollate as a base would not be appreciable at this hydroxyl ion concentration; hence the method becomes a quantitative one.

Neutralization Curves for the Different Amino Acids.—In Fig. 2 will be found the curves showing the course of neutralization for the substances used in this investigation. The curve for glycollol is quite symmetrical and shows the influence of the amino group on the neutralization of the carboxyl. The acidic nature of the benzene ring is shown very clearly by the curve for phenylalanin. Not only is the initial P_H value greater than that of glycollol, but the curve of neutralization lies above that of glycollol for the entire distance.

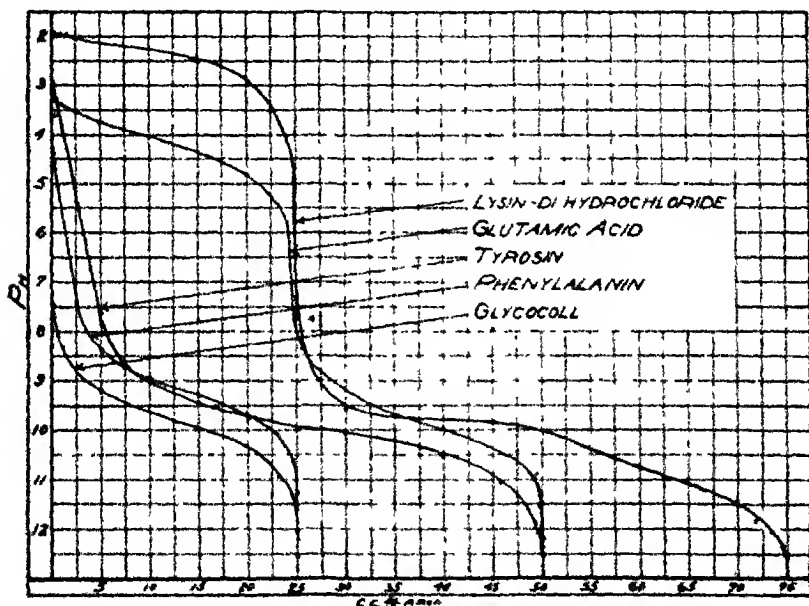


Fig. 2.—Neutralization curves for amino acids alone.

In the curve for glutamic acid the influence of the second carboxyl group can be clearly seen. One carboxyl group is neutralized above the concentration P_H 7; while the other is below this point. The influence of the amino group on the nearest carboxyl makes an enormous difference on the concentration of the hydroxyl ion necessary to neutralize it, as compared with that for the carboxyl further away from the amino group.

Since it was desired to see what influence the combined hydrochloric acid would have on the neutralization curve, no correction was made for the combined acid in lysine dihydrochloride. It will be noticed that

about $\frac{1}{3}$ of the acidity is neutralized before the value P_H 7.0 is reached and $\frac{2}{3}$ below this point. This would indicate that the strongly negative chlorine influences the molecule to such an extent that lysine dihydrochloride ionizes as a strong acid. Since both amino groups are combined with hydrogen chloride, the carboxyl will be neutralized above the P_H 7.0 point. An excess of hydroxyl ions are necessary, however, to split off the combined hydrogen chloride groups.

As might be expected, the tyrosin molecule behaves as a dibasic acid. A greater hydroxyl ion concentration, however, is required for complete neutralization than in the case of the simpler amino acids.

A comparison of the neutralization curve of tyrosin with that of phenylalanin shows the increased acidic property imparted by the hydroxyl groups in the benzene ring.

Summary.

1. By means of the above adaptation of the electrometric titration method it is possible to obtain the neutralization curves of amino acids alone. In this way the influence of the different groups in the molecule can be seen and certain inaccuracies in the formal titration method explained by definite data.

2. An hydroxyl ion concentration of about 2×10^{-3} (P_H 12.5) will suppress to a negligible quantity the basic ionization of the sodium salts of the amino acids, and thus make possible a more exact quantitative determination of the diamino acids as well as that of others containing strongly negative groups.

3. The quantitative method is carried out as follows. Sufficient standard alkali is added to a definite volume of the aqueous solution of the amino acid under investigation to give it a P_H value of about 12.5. Then to an equal volume of water, the same standard alkali is added in an amount sufficient to give it the same P_H value, care being taken to add sufficient water to give the blank the same volume as that of the original at the P_H value compared. Subtracting the cc. used in the blank from that required in the original gives the cc. of standard alkali necessary to neutralize the amino acid alone.

MANRATYAN, KANSAS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]
HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS: THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS. VI. A STUDY OF THE IONIZATION RELATIONS OF SODIUM AND POTASSIUM CHLORIDES, BROMIDES AND IODIDES IN MIXTURES.

BY L. S. WELLS AND G. MCP. SMITH.¹

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A. Introduction.

This investigation is a study of the equilibrium between mixed sodium and potassium salts and liquid amalgams, with free mercury present in such quantity that its active mass may be taken as constant, as represented by the equation,

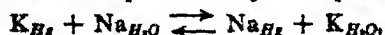


in which NaX and KX represent the dissolved halides, chloride, bromide, or iodide. The investigation is the sixth of a series on this subject,² and its especial object is to study the influence exerted by the anions on the constitution of aqueous halide solutions.³

It has been shown in earlier papers of this series that in equivalent mixtures of sodium and potassium chlorides, the sodium ion fraction gains upon that of the potassium as the concentration is increased. Analogous observations have been made, to an even greater degree, in the present investigation, which, in addition to the chlorides, includes the bromides and iodides of sodium and potassium. These ion-fraction changes may be due to any or all of the following causes: the existence of intermediate ions, of hydrated ions, and of complex ions.

B. Theoretical.

Since only the free atoms and ions of the metals are supposed to take a direct part in the reaction represented by the equation,

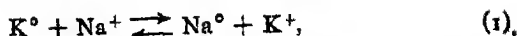


we must re-state the equilibrium in terms of the equation,

¹ From a thesis submitted to the Graduate School of the University of Illinois by Lansing Sadler Wells in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry.

² G. MCP. Smith, *THIS JOURNAL*, 32, 502 (1910); 35, 30 (1913); Smith and Ball, 39, 179 (1917); Smith and Braley, 39, 1545 (1917); Smith and Rees, 40, 1802 (1918).

³ The failure of the application of the different methods of determining the degree of ionization, namely the methods involving colligative properties, and also the conductivity method of Arrhenius, may be attributed to the occurrence of complex chemical processes between the different ionic and molecular species in solution, the nature, or, at any rate, the extent of which is by no means well known (cf. Smith and Rees, *Loc. cit.*).



in which K° and Na° represent the free atoms of potassium and sodium in the mercurial phase, and Na^{+} and K^{+} the simple, free ions in the aqueous phase. And this equilibrium may be formulated into the following mass-law expression:

$$\frac{(K^{\circ})(Na^{+})}{(Na^{\circ})(K^{+})} = k, \text{ or } C_e,^1 \quad (2)$$

in which (K°) and (Na°) are the mol. fractions of free, uncombined potassium and sodium in the mercurial solution, and (K^{+}) and (Na^{+}) the simple ion fractions of these metals in the aqueous solution.

A liquid alkali amalgam contains, as the solute, a compound of the general formula $MeHg_x$,² but, even so, the alkali metal in such an amalgam possesses a solution tension, or tendency to enter into aqueous solution in the ionic condition. The solute in these amalgams must, therefore, be very slightly dissociated, in the sense of the equation,



for which the mass-law expression is

$$\frac{(Me^{\circ})(Hg)^x}{(MeHg_x)} = \text{const.}$$

Or, in the very dilute amalgams, in which the active mass of free mercury is constant, we have

$$\frac{(Na^{\circ})}{(NaHg_n)} = \text{const.}, \text{ and } \frac{(K^{\circ})}{(KHg_m)} = \text{const.}$$

Assuming that these expressions hold true in amalgams containing both metals, we obtain

$$\frac{(K^{\circ})}{(Na^{\circ})} = \frac{(KHg_m)}{(NaHg_n)} = \frac{(K^{\circ}) + (KHg_m)}{(Na^{\circ}) + (NaHg_n)} = \frac{(K_{Hg})}{(Na_{Hg})}, \quad (4)$$

and, substituting in Equation 2, for $\frac{(K^{\circ})}{(Na^{\circ})}$, the value $\frac{(K_{Hg})}{(Na_{Hg})}$, we obtain the expression

$$\frac{(K_{Hg})(Na^{+})}{(Na_{Hg})(K^{+})} = k. \quad (5)$$

Now, in any individual mixed salt solution, the ratio of the salt fractions must bear some numerical relationship to the ion-fraction ratio, or

$$\frac{(NaX)}{(KX)} = n \frac{(Na^{+})}{(K^{+})}, \quad (6)$$

¹ It is thought advisable to return to the letter k (or K), as in the original formulae in place of the symbol C_e which was used for a special reason in the third and fourth papers of the series (cf. Smith and Rees, *Loc. cit.*, p. 1808, footnote).

² Cf. G. McP. Smith, *Z. anorg. Allgem. Chem.*, 52, 381 (1908); 52, 161 (1914).

in which the value of n is unknown and may, of course, vary with the conditions of salt concentration. But, whatever the value of n may be at any specific composition of the aqueous mixture, it follows from the preceding equations that, in the case of any particular equilibrium mixture,

$$\frac{(K_{H_2})(NaX)}{(Na_{H_2})(KX)} = n.k = C_e. \quad (7)$$

The values of (K_{H_2}) and (Na_{H_2}) may readily be calculated from the analytical data of the equilibrium amalgams, and (NaX) and (KX) are known concentration fractions of sodium and potassium chloride, bromide, or iodide. Thus it is possible to calculate C_e , the "equilibrium expression" at any specific salt concentration.

By definition,

$$(Na^+) + (K^+) = 1.$$

Combining this with Equation 5, and solving, we get

$$(K^+) = \frac{(K_{H_2})}{(K_{H_2}) + k(Na_{H_2})}. \quad (8)$$

If, therefore, a means could be found of obtaining the value of k , we should be in a position to calculate the actual ion-fraction values, (Na^+) and (K^+) , in the various mixed solutions.

C. Experimental Details.

1. **Materials and Apparatus.**—In addition to the apparatus and materials used in the preceding investigations, and there described, the following are used for the first time in this investigation:

(a) *Sodium Bromide, NaBr.2H₂O.*—The pure commercial salt was recrystallized from hot distilled water. The mother liquor was removed as completely as possible by suction, after which the remainder was thrown off in a high speed electrical centrifuge. A second crystallization was made from pure water, and the mother liquor removed as before. After this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

(b) *Potassium Bromide.*—A good grade of commercial salt was recrystallized twice from hot water, as described above. The salt was then dried in a platinum dish in an electric oven at 150°. Just before use it was heated in the dish in an electric muffle furnace for at least two hours at a temperature just short of fusion. It was cooled in a desiccator over calcium chloride.

(c) *Sodium Iodide, NaI.2H₂O.*—The pure commercial salt was recrystallized three times from hot water, as described in the purification of sodium bromide. After this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

(d) *Potassium Iodide*.—A pure grade of commercial salt was recrystallized two or three times from hot water. The samples were then dried in an electric oven for several hours at 150°, and finally placed in tightly stoppered bottles.

2. **Method of Experimentation.** (a) *Solutions*.—Separate solutions of the NaX and KX (in which X represents Cl, Br, or I) were made up, each equal in concentration to the total concentration of the mixed solution desired. By mixing these solutions in the proper volume relations, solutions of any salt concentration ratio desired, and of the given total salt concentration, were prepared.

In the case of the sodium chloride, potassium chloride, or potassium bromide, the pure dried salt was weighed out in the calculated quantity, dissolved in pure water, and the solution transferred to a calibrated volumetric flask, in which it was diluted to the mark at 25°. In the case of the potassium iodide, sodium iodide, or sodium bromide, the salt was weighed out in sufficient quantity to give a solution slightly more concentrated than desired. The normality of the solution so prepared was determined by the Volhard volumetric method, and it was then accurately diluted to the desired normality.

(b) *Equilibrium*.—In order that, at the start of each run, the amalgams should be as nearly as possible of the same concentration, the analyzed stock amalgams were diluted with mercury to the specific concentration desired. These amalgams were then brought into equilibrium with the solution under investigation, as described in the previous paper. The amalgam was in each case finally washed with water, and decomposed with hydrochloric acid, according to the procedure described in an earlier paper.¹

Each run was made with 6 separate reaction mixtures, 3 of which were started with sodium amalgam and 3 with potassium amalgam; in all 6, identical mixed salt solutions were used. Equilibrium was, therefore, approached 3 times from each side.

(c) *Treatment of the Decomposition Products*.—The hydrochloric acid solution containing the alkali metals from the equilibrium amalgam was in each case quantitatively removed from the mercury and evaporated to dryness on the steam bath. The mercury itself was dried, and weighed to within 0.1–0.2 g. The mixed alkali chlorides were weighed and analyzed as described in a previous paper.²

D. Experimental Data.

The data obtained in this investigation are recorded in the following tables: In Table I, which is given in full to show the data in detail, as

¹ Smith and Ball, *Loc. cit.*

² Smith and Ball, *Ibid.* The above procedure differs from that of Smith and Ball, in that the concentration of the equilibrium amalgams was accurately determined.

well as to afford an indication of the degree of accuracy attained,¹ the figures in the first column refer to the number of the experiment; the second column indicates the amalgam used at the start; the third, fourth and fifth columns contain the data, in grams, obtained by the analysis of the amalgam after the establishment of equilibrium between it and a solution of the composition given at the top of the table. Thus Col. 3 gives the weight of the mixed alkali chlorides; Col. 4 the weight of potassium chloroplatinate obtained in the analysis of the mixed chlorides; and Col. 5 the weight of the mercury in the equilibrium amalgam. Col. 6 shows the concentration of the equilibrium amalgam in total milli-equivalents of alkali metals per 10 g. of mercury, as calculated from the data in Cols. 3, 4 and 5; Cols. 7 and 8 give the mol. fractions of the amalgamated metals in the mercurial phase at equilibrium, as calculated from Cols. 3 and 4; and Col. 9 gives the value of the expression

$$\frac{(K_{H_2})(NaX)}{(Na_{H_2})(KX)} = n.k = C_e,$$

in which (K_{H_2}) and (Na_{H_2}) are the respective mol fractions in the mercurial phase, from Cols. 7 and 8, and (NaX) and (KX) are the known mol fractions of the halides in the aqueous phase.

In the light of the above description the subsequent tables, which contain the results in abbreviated form, will be self-explanatory.

1. Effect of Varying the Concentration of the Mercurial Phase at a Fixed (Equivalent) Salt-Concentration Ratio and a Fixed Normal Concentration of the Aqueous Phase.—In the sodium-potassium equilibrium, the sodium-strontium equilibrium, and the potassium-strontium equilibrium, it has previously been observed that the total concentration of the mercurial phase exerts a marked effect on the equilibrium value C_e . In the case of the sodium-strontium equilibrium the C_e value was found to be a linear function of the amalgam concentration.² In the potassium-strontium equilibrium it was found that the C_e value increases directly with the amalgam concentration up to about 0.3 milli-equivalent of metals per 10 g. of mercury.³ In all 3 equilibria studied it has been observed that when highly concentrated liquid amalgams are used the values of C_e obtained are apt to be erratic.

When it was first realized that the concentration of the liquid amalgams was a factor of moment, a study was made of the question by diluting the original amalgams with varying amounts of mercury, in a series of determinations, and then bringing them to equilibrium, at 25°, with a 0.2 *N*

¹ The most consistent values are obtained with amalgams which contain 0.15–0.30 milli-equivalents of metals per 10 g. of Hg; for this reason, beginning with Table IV, the amalgams used were all of this approximate concentration

² Smith and Braley, *Loc. cit.*

³ Smith and Braley, *Loc. cit.*

equivalent mixture of sodium and potassium chlorides;¹ but, owing to the incomplete nature of this first study, it has seemed desirable to investigate the question further.

TABLE I.

The Effect of Varying the Concentration of the Mercurial Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature, 25°.					NaCl : KCl.				
Expt No.	Amalgam at start	Analysis of the equilibrium amalgam.		Hg.	Milli-equiv of metals per 10 g Hg	Mol fractions of amalgamated metals.			
		NaCl + KCl.	K ₂ PtCl ₆ .			Na.	K.	Ce.	
1.....	Na	0.2118	0.2353	57.3	0.586	0.713	0.287	0.403	
2.....	Na	0.1860	0.2090	50.7	0.581	0.709	0.291	0.411	
3.....	Na	0.2180	0.2407	57.6	0.600	0.715	0.285	0.397	
4.....	K	0.2091	0.2300	55.2	0.601	0.715	0.285	0.398	
5.....	K	0.2137	0.2368	56.3	0.602	0.713	0.287	0.401	
6.....	K	0.1915	0.2111	51.0	0.596	0.715	0.285	0.398	
Mean, 0.594								0.401	
7.....	Na	0.2018	0.2367	109.5	0.291	0.695	0.305	0.438	
8.....	Na	0.2055	0.2403	107.7	0.301	0.696	0.303	0.435	
9.....	Na	0.2181	0.2544	113.2	0.304	0.698	0.302	0.433	
10.....	K	0.2143	0.2515	115.9	0.285	0.696	0.304	0.436	
11.....	K	0.2299	0.2698	118.1	0.307	0.695	0.305	0.439	
12.....	K	0.2133	0.2491	108.8	0.309	0.697	0.303	0.435	
Mean, 0.299								0.436	
13.....	Na	0.1843	0.2210	198.2	0.146	0.688	0.312	0.453	
14.....	Na	0.1990	0.2379	197.4	0.159	0.689	0.311	0.451	
15.....	Na	0.2069	0.2476	197.4	0.165	0.689	0.311	0.451	
16.....	K	0.2240	0.2720	199.0	0.177	0.684	0.316	0.462	
17.....	K	0.2265	0.2715	201.0	0.177	0.688	0.312	0.453	
18.....	K	0.2310	0.2773	199.6	0.182	0.688	0.312	0.453	
Mean, 0.168								0.454	
19.....	Na	0.2091	0.2551	261.8	0.126	0.684	0.316	0.462	
20.....	Na	0.1650	0.1957	256.8	0.101	0.692	0.308	0.445	
21.....	Na	0.1575	0.1868	261.2	0.095	0.689	0.311	0.452	
22.....	K	0.2176	0.2648	262.9	0.130	0.685	0.315	0.459	
23.....	K	0.2311	0.2790	279.2	0.130	0.686	0.314	0.457	
24.....	K	0.1694	0.2039	253.6	0.105	0.686	0.314	0.456	
Mean, 0.115								0.455	
25.....	Na	0.2101	0.2546	557.1	0.0593	0.684	0.316	0.461	
26.....	K	0.2152	0.2627	573.5	0.0586	0.683	0.317	0.463	
27.....	K	0.2033	0.2463	554.0	0.0573	0.688	0.311	0.453	
28.....	K	0.2171	0.2594	560.5	0.0617	0.687	0.313	0.455	
Mean, 0.0592								0.458	

¹ Smith and Ball, *Loc. cit.*

¹ Smith and Ball, *Loc. cit.*

The data for this study are given in Table I. In this series of experiments, with equivalent sodium and potassium chloride mixtures at a total concentration of 0.2 *N*, the concentration of the amalgams was decreased in each successive run.

It is to be noted that the mean values of the "equilibrium expression," C_e , obtained in the different runs increase with decreasing amalgam concentration. In any one run, the equilibrium amalgams of the individual mixtures were always found to differ somewhat in concentration; because, in the first place, the stock amalgams were weighed out more or less roughly for dilution, and, in the second place, evolution of hydrogen (always in evidence to a very slight extent, at best) varied somewhat in the individual experiments.

However, in the case of this equilibrium, the values of C_e are not influenced enough by the slight differences of amalgam concentration in the individual experiments of a run to warrant a correction, as in the case of the sodium-strontium, or of the potassium-strontium equilibrium.

Table II contains data showing the effect of varying the amalgam concentration, but with equivalent sodium and potassium chloride mixtures of 0.2, 0.5, 1.0, 2.0, and 4.0 *N* concentration, respectively.

In Fig. 1, the values of C_e as ordinates, are plotted against the total amalgam concentration in milli-equivalents of metals per 10 g. of mercury. Each point indicated in the plot is the average of about 6 separate determinations.

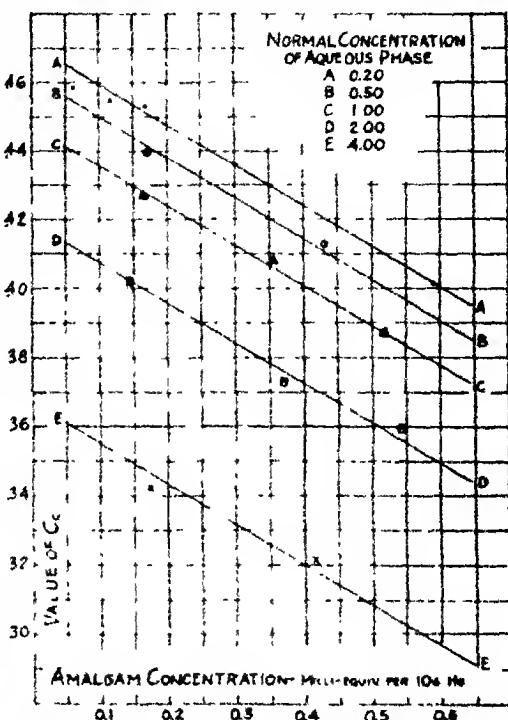


Fig. 1.—Showing the value of C_e as a function of amalgam concentration, at different salt concentrations, NaCl : KCl.

Temperature, 25°.

TABLE II

The Effect of Varying the Concentration of the Mercurial Phase at Various Fixed (Equivalent) Concentrations of the Aqueous Phase.

Temperature 25°

NaCl : KCl.

Mean values of Expts. No	Amalgam at start	Milli equiva- lents of metals per 10 g Hg	Mol fractions of amalgamated metals		C_c
			Na	K	
Mixed Aqueous Phase 0.2 N (see Table I)					
		Mean, 0.594	0.713	0.287	0.401
		Mean, 0.299	0.696	0.314	0.436
		Mean, 0.168	0.688	0.312	0.454
		Mean, 0.115	0.687	0.313	0.455
		Mean, 0.0592	0.685	0.314	0.458
Mixed Aqueous Phase 0.5 N					
1-3	Sodium	0.435	0.708	0.292	0.412
4-6	Potassium	0.426	0.707	0.293	0.414
	Mean, 0.430				0.413
7-9	Sodium	0.170	0.695	0.305	0.439
10-12	Potassium	0.174	0.694	0.305	0.440
	Mean, 0.172				0.439
Mixed Aqueous Phase 1.0 N					
13-15	Sodium	0.504	0.720	0.280	0.388
16-18	Potassium	0.527	0.722	0.278	0.386
	Mean, 0.515				0.387
19-21	Sodium	0.352	0.710	0.290	0.408
22-24	Potassium	0.357	0.710	0.289	0.408
	Mean, 0.354				0.408
25-27	Sodium	0.162	0.701	0.299	0.427
28-30	Potassium	0.166	0.700	0.300	0.427
	Mean, 0.164				0.427
Mixed Aqueous Phase 2.0 N					
31-33	Sodium	0.537	0.735	0.265	0.360
34-36	Potassium	0.541	0.735	0.265	0.360
	Mean, 0.539				0.360
37-39	Sodium	0.362	0.728	0.272	0.373
40-42	Potassium	0.374	0.729	0.271	0.372
	Mean, 0.368				0.373
43-44	Sodium	0.119	0.710	0.290	0.406
45-47	Potassium	0.159	0.715	0.285	0.398
	Mean, 0.143				0.401
Mixed Aqueous Phase 4.0 N					
48-50	Sodium	0.412	0.757	0.243	0.320
51-53	Potassium	0.420	0.756	0.244	0.322
	Mean, 0.416				0.321
54-56	Sodium	0.178	0.745	0.255	0.343
57-59	Potassium	0.173	0.746	0.254	0.342
	Mean, 0.175				0.342

2. Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio and at Various Specific Amalgam Concentrations.—Table III contains data showing the effect of increasing the total salt concentration in stages from 0.2 *N* to 4.0 *N*, the salts (sodium and potassium chlorides) being present in equivalent proportions, at various fixed amalgam concentrations. The values of C_e in this table were obtained by simply reading them from the plots in Fig. 1, at the indicated amalgam concentrations.

Fig. 2 illustrates the effect upon the C_e value, at different specific amalgam concentrations, of varying the normality of the aqueous phase in the case of equivalent sodium and potassium chloride mixtures. From this series of plots it appears that a change in concentration of 0.1 milli-equivalent of metals

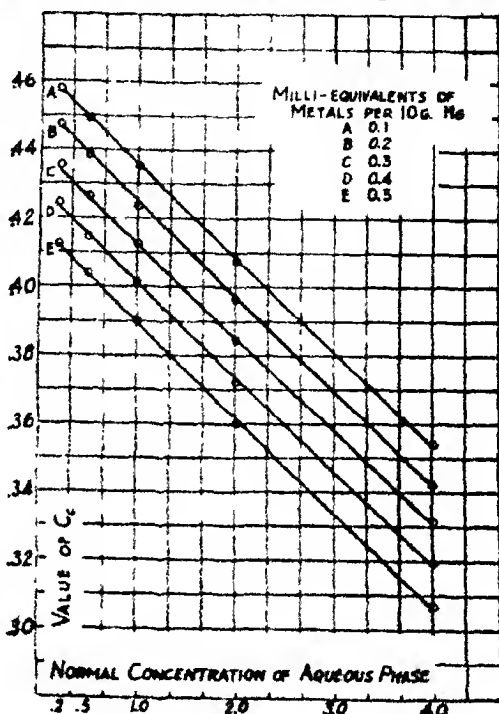


Fig. 2.—Showing the value of C_e as a function of total salt concentration, at different amalgam concentrations. NaCl : KCl Temperature, 25°.

TABLE III
The Value of C_e as a Function of Total Salt Concentration at a Fixed Equivalent Salt-Concentration Ratio and at Various Specific Amalgam Concentrations.
Temperature 25°. NaCl:KCl.

Normality of aqueous phase.	C_e values at x milli-equivalents of metals per 10 g. of mercury.				
	$x = 0.1$.	$x = 0.2$	$x = 0.3$.	$x = 0.4$.	$x = 0.5$.
0.2	0.458	0.447	0.435	0.424	0.412
0.5	0.449	0.438	0.426	0.415	0.403
1.0	0.435	0.423	0.412	0.401	0.389
2.0	0.408	0.396	0.384	0.373	0.360
4.0	0.354	0.342	0.331	0.319	0.308

3. Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.—If the

reaction between alkali metal amalgams and alkali salt solutions is ionic, the mass-law expression,

$$\frac{(K_{Hg})(Na^+)}{(Na_{Hg})(K^+)} = k,$$

demands that the value of k should remain constant, regardless of the relative concentrations of the simple sodium and potassium ions; on the other hand, however, constancy is not necessarily demanded in the value of C_c in the equation,

$$\frac{(K_{Hg})(NaX)}{(Na_{Hg})(KX)} = n k = C_c.$$

The results of previous experiments carried out in this laboratory with undiluted liquid sodium and potassium amalgams show "that if the total concentration of the solution remains constant, the value of C_c is constant even though the mol fractions of the two salts in the mixtures vary over wide limits. . . . When diluted amalgams and more concentrated aqueous solutions were employed, a slight change in the value of C_c could be observed as the ratio of the salt concentrations was varied."¹

TABLE IV
The Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.

Temperature 25°					
Mixed Aqueous Phase 0.2 N					
Mean values of Expts No.	Amalg. concn. at start	Milli equivalents of metals per 10 g. Hg	Mol fractions of amalgamated metals		C_c
			Na	K	
<i>2 NaCl:KCl</i>					
1-3	Sodium	0.175	0.616	0.184	0.452
4-6	Potassium	0.176	0.815	0.185	0.453
Mean, 0.175					0.452
<i>NaCl:KCl</i>					
See Table I, Expts. 13-18					
Mean, 0.168					0.454
<i>NaCl:2 KCl</i>					
7-9	Sodium	0.171	0.526	0.474	0.431
10-12	Potassium	0.175	0.522	0.478	0.457
Mean, 0.173					0.454
Mixed Aqueous Phase 1.0 N					
<i>2 NaCl:KCl</i>					
13-14	Sodium	0.178	0.823	0.177	0.431
15-17	Potassium	0.178	0.821	0.179	0.436
Mean, 0.178					0.434
<i>NaCl:KCl</i>					
See Table II, Expts. 23-30					
Mean, 0.164					0.437
Smith and Ball, <i>Loc. cit.</i>					

¹ Smith and Ball, *Loc. cit.*

Table IV contains the results obtained upon varying the ratio of sodium and potassium chlorides at a total concentration of 0.2 *N*, and at a total concentration of 1.0 *N*. These experiments show that within the experimental error, the value of C_c is constant when dilute amalgams and rather dilute aqueous solutions are employed. With the more concentrated aqueous solution, there appears to be a slight difference between the values of C_c obtained with a salt ratio of NaCl:KCl and those obtained with a ratio of 2 NaCl:KCl, but this difference really falls within the limit of accuracy of the latter run. These results are in accordance with, and confirmatory of, results obtained in the earlier investigations of the series.

4. Effect of Varying the Normal Concentration of Equivalent Sodium and Potassium Chloride, Bromide, or Iodide Mixtures at a Fixed Amalgam Concentration.—In a previous study of the effect of increasing the total salt concentration in sodium and potassium chloride mixtures, at a fixed salt-concentration ratio, it was found¹ that upon raising the salt concentration the value of C_c decreases. This study was later extended and now includes mixtures of sodium and potassium sulfates and chlorides,² sodium and strontium chlorides,³ and potassium and strontium chlorides.⁴ It has seemed desirable to further extend the investigation to include equivalent aqueous mixtures of sodium and potassium chlorides, bromides and iodides.

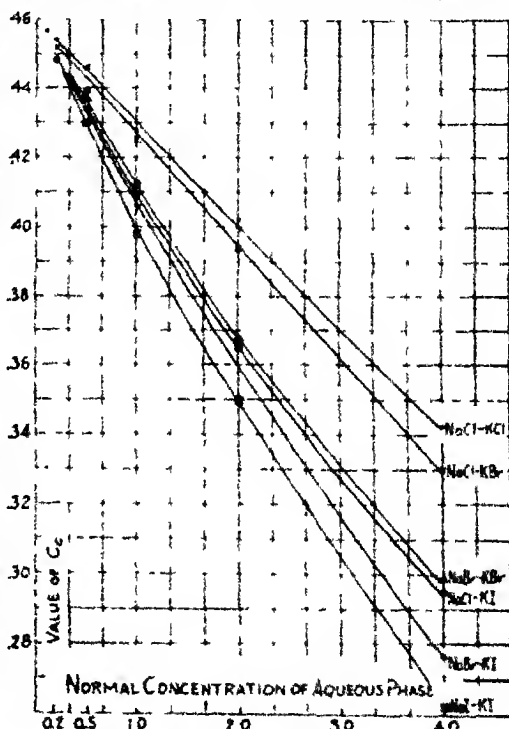


Fig. 3.—Showing the value of C_c as a function of total salt concentration, for various mixtures. Temperature, 25°.

¹ G. McP. Smith, *THIS JOURNAL*, 35, 39 (1915).

² Smith and Ball, *Loc. cit.*

³ Smith and Braley, *Ibid.*

⁴ Smith and Ross, *Ibid.*

The data for this study are given in Tables V, VI, VII, VIII, IX and X. The total concentration of the equivalent mixtures was increased from 0.1 *N* to 4.0 *N* for each salt mixture, with the exception of the sodium bromide-potassium iodide and sodium iodide-potassium iodide mixtures, with which the concentration was increased from 0.2 *N* to 4.0 *N*. In all of the individual experiments of each run, the amalgams were diluted to the same approximate concentration (about 0.2 milli-equivalent of metal per 10 g. of mercury). While the final concentration of the equilibrium amalgam was slightly less than this, the small individual differences in concentration do not warrant a correction of the C_c values. In every equilibrium studied, the value of C_c decreases with increasing concen-

TABLE V
The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed
(Equivalent) Salt Concentration Ratio.

Temperature 25°

NaCl:KCl

Mean values of Expts No	Amalgam at start	Mills equivalents of metals per 10 g. Hg	Mol. fractions of amalgamated metals		C_c
			Na	K	
Mixed Aqueous Phase 0.1 <i>N</i>					
1-2	Sodium	0.140	0.689	0.311	0.451
3-5	Potassium	0.151	0.688	0.312	0.454
					0.453
Mean, 0.147					
Mixed Aqueous Phase 0.2 <i>N</i>					
See Table I, Expts 13-18					
					0.454
Mean, 0.168					
Mixed Aqueous Phase 0.5 <i>N</i>					
See Table II, Expts 7-12					
					0.439
Mean, 0.172					
Mixed Aqueous Phase 1.0 <i>N</i>					
See Table II, Expts 25-30					
					0.427
Mean, 0.164					
Mixed Aqueous Phase 1.983 <i>N</i> . ^a (0.983 NaCl:KCl)					
6-8	Sodium	0.166	0.710	0.290	0.401
9-11	Potassium	0.172	0.709	0.291	0.403
					0.402
Mean, 0.168					
Mixed Aqueous Phase 2.0 <i>N</i>					
See Table II, Expts 43-47					
					0.402
Mean, 0.143					
Mixed Aqueous Phase 4.0 <i>N</i>					
See Table II, Expts. 54-59					
					0.342
Mean, 0.175					

The normality ratios in Expts 6-11 of the

0.342

^a The normality ratios in Expts 6-11 of this table are 0.983 NaCl to 1.000 KCl, instead of 1.000 to 1.000 as was intended. The error in the NaCl solution was detected only after the completion of the run. The values of 0.983 *N* NaCl and 1.000 *N* KCl were used in calculating C_c . Table II, Expts 43-47, gives the run as repeated, with NaCl:KCl, at a total concentration of 2.0 *N*.

tration of the mixed salt solution. The results are best studied by means of the curves in Fig. 3, in which the C_c values are plotted against the total normal salt concentrations. It will be observed that the C_c values change the more rapidly, the higher the atomic weight of the halogen.

TABLE VI

The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio

Temperature 25°.			NaCl:KBr		
Mean values of Expts No.	Amalgam at start	Milli-equiva- lents of metals per 10 g Hg	Mol fractions of amalgamated metals		C_c
			Na	K	
Mixed Aqueous Phase 0.1 N					
1- 3	Sodium	0.151	0.682	0.318	0.466
4- 6	Potassium	0.161	0.686	0.313	0.455
Mean, 0.156					0.461
Mixed Aqueous Phase 0.2 N					
7- 9	Sodium	0.177	0.689	0.311	0.451
10-12	Potassium	0.175	0.686	0.313	0.456
Mean, 0.176					0.453
Mixed Aqueous Phase 0.5 N					
13-15	Sodium	0.180	0.692	0.308	0.445
16-18	Potassium	0.179	0.692	0.308	0.445
Mean, 0.180					0.445
Mixed Aqueous Phase 1.0 N					
19-21	Sodium	0.179	0.699	0.301	0.430
22-24	Potassium	0.178	0.700	0.300	0.429
25-27	Sodium	0.177	0.704	0.296	0.421
28-30	Potassium	0.179	0.704	0.296	0.421
Mean, 0.178					0.423
Mixed Aqueous Phase 2.0 N					
31-32	Sodium	0.188	0.715	0.285	0.397
33-35	Potassium	0.191	0.717	0.283	0.394
Mean, 0.190					0.395
Mixed Aqueous Phase 4.0 N					
36-38	Sodium	0.192	0.750	0.250	0.331
39-41	Potassium	0.188	0.752	0.247	0.329
Mean, 0.190					0.330

5. The Ion-fraction Changes which Take Place upon Increasing the Concentration of Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides, and Iodides.—In the theoretical section, it has been shown that, given the value of k (Equation 5), the ion fractions

TABLE VII
The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed
(Equivalent) Salt-Concentration Ratio.

Temperature 25°.

NaCl:KI.

Temperature 25°.		Mol. fractions of amalgamated metals			C _c .
Mean values of Expts. No	Amalgam at start	Multi equivalents of metals per 10 g Hg	Na.	K.	
Mixed Aqueous Phase 0.1 N.					
1-3	Sodium	0.161	0.685	0.315	0.460
4-6	Potassium	0.164	0.688	0.312	0.453
7-9	Sodium	0.158	0.686	0.314	0.457
10-12	Potassium	0.156	0.685	0.315	0.460
Mean, 0.159					0.457
Mixed Aqueous Phase 0.2 N.					
13-15	Sodium	0.171	0.687	0.313	0.455
16-17	Potassium	0.177	0.690	0.309	0.448
Mean, 0.174					0.452
Mixed Aqueous Phase 0.5 N.					
18-20	Sodium	0.173	0.701	0.299	0.427
21-23	Potassium	0.172	0.697	0.302	0.433
Mean, 0.173					0.430
Mixed Aqueous Phase 1.0 N.					
24-26	Sodium	0.177	0.710	0.290	0.408
27-29	Potassium	0.175	0.709	0.290	0.410
Mean, 0.176					0.409
Mixed Aqueous Phase 2.0 N.					
30-32	Sodium	0.187	0.733	0.267	0.364
33-35	Potassium	0.179	0.733	0.267	0.365
Mean, 0.183					0.365
Mixed Aqueous Phase 4.0 N.					
36-38	Sodium	0.187	0.773	0.227	0.293
39-41	Potassium	0.186	0.770	0.230	0.298
Mean, 0.187					0.295

of the metals in the individual aqueous mixtures may be calculated by means of the expressions.

$$(K^+) = \frac{(K_{Hg})}{(K_{Hg}) + k.(Na_{Hg})}$$

and

$$(Na^+) = 1 - (K^+).$$

But, since we do not know either the respective degrees of dissociation of the sodium and potassium hydrargyrides in the mercurial phase, or the simple (unhydrated) ion fractions of these metals in the aqueous

TABLE VIII.
The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed
(Equivalent) Salt-Concentration Ratio
Temperature 25°.

Temperature 25°.

(Equivalents per Cent Concentration Basis)

NaBr:KBr.

Mean values of Expts. No	Amalgam at start	Milli-equi- valents of metals per 10 g. Hg.	Mol fractions of amalgamated metals		C _c .
			Na	K	
Mixed Aqueous Phase 0.1 N.					
1-3	Sodium	0.153	0.687	0.313	0.456
4-6	Potassium	0.157	0.687	0.313	0.456
Mean, 0.155					0.456
Mixed Aqueous Phase 0.2 N.					
7-9	Sodium	0.172	0.691	0.309	0.447
10-12	Potassium	0.176	0.689	0.311	0.451
Mean, 0.174					0.449
Mixed Aqueous Phase 0.5 N.					
13-15	Sodium	0.175	0.696	0.304	0.437
16-18	Potassium	0.176	0.695	0.305	0.438
Mean, 0.176					0.437
Mixed Aqueous Phase 1.0 N.					
19-21	Sodium	0.175	0.708	0.292	0.412
22-24	Potassium	0.179	0.709	0.291	0.411
Mean, 0.177					0.412
Mixed Aqueous Phase 2.0 N.					
25-27	Sodium	0.173	0.731	0.269	0.367
28-29	Potassium	0.176	0.732	0.268	0.367
Mean, 0.175					0.367
Mixed Aqueous Phase 4.0 N.					
30-32	Sodium	0.190	0.769	0.231	0.301
33-35	Potassium	0.190	0.770	0.230	0.298
Mean, 0.190					0.299

phase, there does not seem to be any prospect for the determination of the value of k . We are, therefore, compelled to start with some assumption concerning the value of k , in order, with that as a basis, to study the *ion-fraction changes* which accompany changes in salt-concentration in the aqueous phase.

With the assumption as a starting point that in each of the equivalent sodium and potassium salt mixtures at a total concentration of 0.2 N, the simple sodium-ion and potassium-ion fractions are 0.500 and 0.500, we can then at least determine, by means of Equation 8, the direction and relative degree of the ion-fraction changes which accompany salt-concentration changes in the aqueous phase. On the basis of the assump-

TABLE IX.
The Effect of Varying the Normal Concentration of the Aqueous Phase as a Fixed (Equivalent) Salt-Concentration Ratio.

NaBr:KI.

Temperature 25°					
Mean values of Expts No	Amalgam at start	Milli-equa- lents of metals per 10 g. Hg.	Mol fractions of amalgamated metals		C ₂
			Na	K	
Mixed Aqueous Phase 0.2 N					
1- 3	Sodium	0 170	0.691	0 309	0.447
4- 6	Potassium	0 173	0 690	0.310	0.449
Mean, 0 172					0.448
Mixed Aqueous Phase 0.5 N					
7- 9	Sodium	0.168	0 697	0 303	0.434
10-12	Potassium	0.173	0 698	0.302	0 432
Mean, 0.171					0.433
Mixed Aqueous Phase 1.0 N.					
13-15	Sodium	0 172	0 711	0 289	0 406
16-18	Potassium	0 175	0 711	0 289	0 406
Mean, 0 173					0 406
Mixed Aqueous Phase 2.0 N.					
19-21	Sodium	0 192	0.736	0 264	0.359
22-24	Potassium	0 184	0 735	0.265	0.361
Mean, 0 188					0 360
Mixed Aqueous Phase 4.0 N					
25-27	Sodium	0 191	0 784	0.216	0.275
28-30	Potassium	0 219	0 783	0.217	0 276
Mean, 0 205					0.276

tion just referred to, the value of k would be equal to that of C_2 at 0.2 N concentration.¹ If, instead of 0.2 N, we should select 0.1 N concentration as the starting point, the results would not be essentially different. The former concentration was selected because (1) the individual values (Na_{H_2}) and (K_{H_2}), calculated on the basis of the mol fractions of sodium

¹ It should be fully realized that k is a real equilibrium constant, and that its value remains the same for all ratios and concentrations of the different mixed salt solutions of sodium and potassium

In assuming a value for k , as a stepping stone in the ion-fraction calculations, we have preferred to assume that in each of the different salt mixtures, at an equivalent salt ratio and at 0.2 N concentration, the ion fractions are equal; rather than to make this assumption in the case of the chloride chloride mixture alone, and to base all the calculations on the k value so obtained. While the former method may appear to involve a contradiction, in that several different k values are assumed, it nevertheless enables us better to compare the ion-fraction changes in the different mixtures, since in every case the calculations are started upon the same basis at 0.2 N concentration.

TABLE X.

The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature 25°			NaI:KI		
Mean values of Expts No	Amalgam at start	Multi-equi- valents of metals per 10 g Hg	Mol fractions of amalgamated metals		C _c
			Na	K	
Mixed Aqueous Phase 0.2 N					
1- 3	Sodium	0 162	0 690	0 310	0 449
4- 6	Potassium	0 160	0 690	0 310	0.448
Mean, 0 161					0 448
Mixed Aqueous Phase 0.5 N					
7- 9	Sodium	0 155	0 699	0 300	0 430
10-12	Potassium	0 174	0 699	0 301	0 431
Mean, 0 165					0 430
Mixed Aqueous Phase 1.0 N					
13-15	Sodium	0 174	0 715	0 285	0.398
16-18	Potassium	0.176	0 715	0 285	0 399
Mean, 0 175					0 398
Mixed Aqueous Phase 2.0 N					
19-21	Sodium	0 179	0.741	0 259	0 350
22-24	Potassium	0 181	0 741	0 259	0 350
Mean, 0 180					0 350
Mixed Aqueous Phase 4.0 N.					
25-27	Sodium	0 182	0 788	0.212	0.270
28-30	Potassium	0.183	0 797	0 203	0 254
Mean, 0 183					0.262

and potassium in the mercurial phase, checked very closely in this case, and (2) runs for all of the salt mixtures were made at this concentration.

The data obtained show clearly that the value of C_c decreases with the increasing concentration of the amalgam, and upon plotting the values of C_c against the values of the total salt concentration (See Fig. 2) for each of 5 different specific amalgam concentrations, a series of 5 parallel curves is obtained; therefore, the statement may be made that the change in value of C_c which is due to the change in amalgam concentration is independent of the change caused by increasing the total salt concentration at a fixed (equivalent) concentration ratio. If this is true, the ion-fraction values found for mixed (equivalent) solutions of sodium and potassium chlorides at specific normal concentrations should be the same regardless of the concentration of the equilibrium amalgam. This conclusion is borne out by the figures in Table XI, which contains

TABLE XI.

The Ion-Fraction Changes which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides at 25°.

Normal concentration of mixed aqueous salt solution	Potassium ion fraction calculated from the C_L value at x milliequivalents of metals per 10 g. Hg, upon the assumption that in the 0.2 Δ equivalent mixture $n = 1$ (Equation 6)		
	$x = 0.1$	$x = 0.3$	$x = 0.5$
0.2	0.500	0.500	0.500
0.5	0.495	0.495	0.495
1.0	0.487	0.486	0.487
2.0	0.470	0.469	0.466
4.0	0.436	0.432	0.429

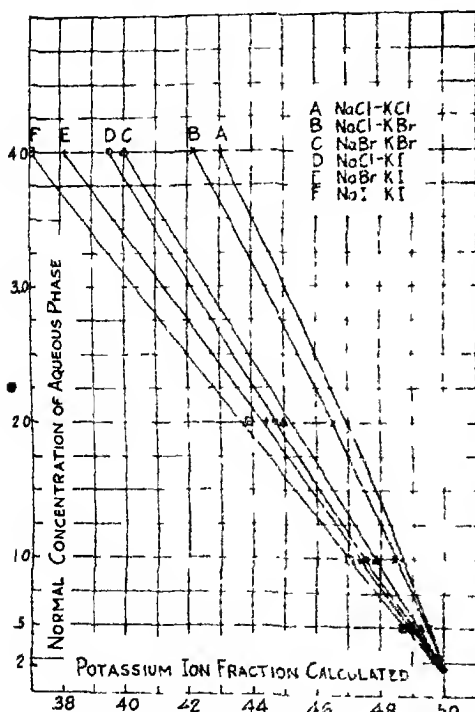


Fig. 4.—Showing the ion fractions of sodium and potassium as a function of total salt concentration, for various mixtures $\text{NaX} \cdot \text{KX}$.

Temperature, 25°.

the potassium-ion fractions calculated at different amalgam concentrations for various equivalent mixtures of sodium and potassium chlorides.

Table XII shows the ion-fraction changes which accompany salt-concentration changes in equivalent aqueous mixtures of sodium and potassium chlorides, bromides, and iodides, at 25°, and in Fig. 4 these values are plotted against the total salt concentration. From these curves it is evident that the potassium-ion fraction decreases, while the sodium-ion fraction correspondingly increases, with increasing total salt concentration. These changes take place the more rapidly, the higher the atomic weight of the halogen.

E. Discussion.

This investigation has shown that, in equivalent, two-salt, aqueous mixtures of the halides of sodium and potassium, the simple potassium-ion fraction (K^+) decreases, while the simple sodium-ion fraction (Na^+) correspondingly increases, with the increasing total concentration of the

TABLE XII.

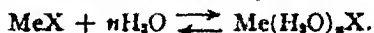
The Ion-Fraction Changes which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides, and Iodides, at 25°.

	Total normal concentration of equivalent aqueous salt mixture.					
	0.1000.	0.2000.	0.5000.	1.000.	2.000.	4.000.
Potassium-ion fractions, calculated at 0.2 milli-equiv. of metals per 10 g. of mer-						
NaCl:KCl	0.499	0.500	0.493	0.485	0.470	0.430
NaCl:KBr	0.504	0.500	0.495	0.484	0.466	0.421
NaCl:KI	0.503	0.500	0.487	0.475	0.447	0.395
NaBr:KBr	0.504	0.500	0.493	0.479	0.450	0.400
NaBr:KI	..	0.500	0.491	0.474	0.445	0.381
NaI:KI	..	0.500	0.490	0.470	0.439	0.370

salts. In the case of the chloride-chloride mixtures, the only halide mixtures of these metals previously investigated, these results agree with and supplement those previously obtained.¹ The results of the present investigation have brought forth the additional fact that, in the equivalent halide mixtures, these same ion-fraction changes take place the more rapidly, the higher the average atomic weight of the halogens in the mixture. The following explanation is offered to account for these phenomena.

1. The Decrease of the Potassium-ion Fraction with Increasing Total Salt Concentration in Equivalent Chloride-chloride Mixtures.—The ion-fraction changes above referred to may be due to either or both of the following causes: (a) the existence of hydrated ions, and (b) the existence of complex ions.

(a) It is well known, for example, that the ions of sodium and potassium are more or less hydrated in solution,² and very likely the non-ionized molecules that furnish these ions also are hydrated, as



It has been pointed out in previous papers of this series³ that such hydrated compounds may also yield intermediate and complex ions, in varying quantities or degrees of stability. There is good evidence that many complexes, not sufficiently stable or insoluble to be isolated, exist in solution. Kendall⁴ has quite recently emphasized the ideas of Werner in regard to the mechanism of the ionization process: "Ionization is preceded by combination between solvent and solute, and is, indeed, a consequence of such combination, and the two phenomena proceed in parallel." Such ideas are in particular harmony with Werner's very

¹ G. McP. Smith, *THIS JOURNAL*, 35, 39 (1913); Smith and Ball, *loc. cit.*

² E. W. Washburn, *Tech. Quart.*, 21, 360 (1908); G. McP. Smith, *THIS JOURNAL*, 37, 722 (1915); Arrhenius, "Theories of Solutions," pp. 184-195.

³ Cf. Smith and Rees, *loc. cit.*

⁴ *THIS JOURNAL*, 39, 2323 (1917).

plausible theory of bases¹ and acids, and with his theory of the formation of higher-order compounds.² Hydration is evidently a case of complex-formation.

(b) Complexes may be formed in other ways than through the agency of water. The alkali halides are capable of forming addition compounds with one another, as well as with other substances, and these may ionize to give complex ions.³ Furthermore, the alkali halides show a tendency to polymerize.⁴ In recent years, evidence (based upon absorption-spectra data) has been adduced which tends to show that the alkali metals, through the agency of secondary valence unions, are capable of effecting closed-ring structures, with the formation of inner-complex salts.⁵ Through conductance studies of the alkali salts of certain organic acids, Lifschitz⁶ has arrived at a similar conclusion.

Evidently, then, since we may have hydrated ions and molecules, addition and polymerized compounds, and many complexes capable of furnishing ions of various species, speculation as to just what specific complexes do exist in these solutions is more or less futile. If, however, as we should expect, potassium has a greater tendency to form complex ions than sodium, then, upon increasing the total concentration of the equivalent aqueous chloride mixtures, the concentration of the simple potassium ion would naturally be decreased more rapidly by mass action than that of the simple sodium ion.

2. The Further Decrease of the Potassium-ion Fraction with Increasing Atomic Weight of the Halogen in the Mixed Salt Solutions.—In the case of chlorine, bromine and iodine, it is well known that the tendency towards complex formation increases with the atomic weight of the halogen. Thus we find iodine forming a great many compounds in which it functions as the central nucleus.⁷

In short, owing to the greater tendency of potassium than of sodium, and of iodine and bromine than of chlorine to form complexes, we should expect the simple potassium-ion fraction to decrease with increasing

¹ Ber., 40, 4133 (1907).

² A. Werner, *Neuere Anschauungen u. d. Gebiete d. anorgan. Chemie*, Braunachweig, 1913.

³ Cf. Werner, *Neuere Anschauungen*, etc., p. 28, Joannis, *Compt. rend.*, 112, 338 (1891); Abegg and Riesenfeld, *Z. physik. Chem.*, 40, 84 (1902).

⁴ Zannovich-Tessarini, *Z. physik. Chem.*, 19, 251 (1896); Andrews and Eade, *Ibid.*, 17, 136 (1895); E. W. Washburn, *Trans. Am. Electrochem. Soc.*, 21, 137 (1912).

⁵ Hantzsch, *Ber.*, 43, 3049 (1910); Hantzsch and Voigt, *Ibid.*, 45, 85 (1912).

⁶ *Z. physik. Chem.*, 87, 567 (1914).

⁷ A. Werner, *Neuere Anschauungen*, etc., L. Gattermann, "The Practical Methods of Organic Chemistry," Macmillan, 1914, p. 244; C. Willgerodt, *Die organischen Verbindungen mit mehrwertigem Jod*, F. Enke, 1914. See also Hantzsch, *Ann.*, 349, 1 (1906); D. McIntosh, *J. Chem. Soc.*, 87, 784 (1905); and K. Hellwig, *Z. anorg. Chem.*, 25, 157 (1900).

total salt concentration; and, also, that this decrease should take place the more rapidly, the higher the average atomic weight of the halogens present.

In conclusion, we may again point out that ionization is most often discussed as if it were a simple dissociation alone, *e. g.*, of the type: $\text{KCl} \rightleftharpoons \text{K}^+ + \text{Cl}^-$, and great emphasis is laid upon the supposition that the mass-law (a law which applies even to the disintegration of radium) is non-applicable to the dissociation of strong electrolytes. Perhaps the mass-law is less at fault than we ourselves, in our inability to determine just what molecular species are present in such solutions, and their individual concentrations.

F. Summary.

1. At a fixed total salt concentration, the value of the equilibrium expression, C_e , decreases with the increasing concentration of the amalgam.
2. At fixed amalgam and total-salt concentrations, but with varying salt ratio, the value of the equilibrium expression, C_e , is constant.
3. At a fixed amalgam concentration, the value of the equilibrium expression, C_e , decreases with the increasing concentration of the mixed (equivalent) salt solution.
4. Ion-fraction calculations are offered for aqueous two-salt mixtures containing the salts in equivalent proportions. It is found that the simple potassium-ion fraction decreases, while the sodium-ion fraction correspondingly increases, with the increasing total salt concentration. These changes take place the more rapidly, the higher the average atomic weight of the halogens in the mixture.

These results are not in harmony with the general conception which prevails in some quarters that, at equivalent concentrations, salts of the same type (*e. g.*, potassium chloride, bromide, iodide, sodium chloride, etc.) are ionized to the same degree.

5. The results of the investigation, insofar as the aqueous salt mixtures are concerned, are readily explainable in terms of A. Werner's theories concerning the formation and dissociation of higher-order compounds.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

THE VAPOR PRESSURE OF AMMONIA.¹

By C. S. CRAGOE, C. H. MEYERS AND C. S. TAYLOR.

Received November 15, 1919

I. Introduction.

The measurements presented in this paper form a portion of the work undertaken by the Bureau of Standards in the determination of the thermal properties of materials used as refrigerating media. The existing data on the vapor-pressure-temperature relation for ammonia are undoubtedly sufficiently accurate to meet the requirements of refrigeration engineering. The Clapeyron equation, however, offers a means of correlating the measurements of the latent heat of vaporization² with the data on specific volumes of saturated liquid and vapor (to be published shortly), provided the slope of the saturation line can be determined with sufficient accuracy. On account of the large errors which may be introduced into the calculated values of the slope by relatively small errors in the pressure or temperature, it appeared that existing data were deficient either in the range or the precision required.

The accuracy of any vapor-pressure measurements is determined in general by 4 factors, namely, (a) purity of the material; (b) certainty of equilibrium conditions; (c) precision of the pressure measuring instrument, and (d) temperature measurement and control.

(a) The extent to which factors (a) and (b) may affect the results of the vapor-pressure measurements will depend upon the methods used. Non-volatile impurities present in solution would affect measurements by the static method and also by the dynamic method if measurements were made of the temperature of the boiling liquid, while their effect on the temperature of the condensing vapor is relatively unimportant. Non-condensing gases have but little effect on measurements by the dynamic method, while in the static method a small amount of non-condensing gas may affect the measured pressure to an extent out of all proportion to the amount of gas present. It is worthy of note that the non-condensing gas does not notably affect the vapor pressure but causes the total pressure as measured by the static method to differ from the true vapor pressure.

(b) In measurements by the static method a very considerable lag in the attainment of equilibrium between the vapor and the liquid may be encountered even with a liquid well freed from impurities, especially if the liquid is not agitated. An example of this is furnished later. The presence of a small amount of permanent gas such as air greatly increases the lag in coming to pressure equilibrium. This was found to be the case

¹ Published by permission of the Director of the Bureau of Standards, Washington, D. C.

² Osborne and Van Dusen, *THIS JOURNAL*, 40, 14 (1918).

at low temperatures as illustrated in an attempt to measure the boiling point of a commercial sample of ammonia by the static method.

(c) The sensitivity of the pressure measuring instruments used in the present work was such as to permit readings of pressure to one part in 5000 or better, except for pressures below one atmosphere. Pressures below 5 atmospheres were measured with mercury manometers, pressures between 5 and 15 atmospheres with a mercury manometer and with a piston gage; pressures above 15 atmospheres with the piston gage only.

(d) Temperature control plays an important rôle in any vapor pressure measurement, particularly in the establishing of equilibrium. A change in the temperature of 0.1° in the case of ammonia is equivalent to a change in the vapor pressure of about 2 mm., 12 mm., and 40 mm. of mercury at -50° , 0° , and $+50^\circ$, respectively, or a percentage change in pressure of about 0.7, 0.4, and 0.25, respectively. The aim in the present experiments was to maintain temperatures constant to 0.01° or better for very long time intervals. Platinum resistance thermometers were employed for the temperature measurements and temperatures were read to thousandths of a degree.

II. Previous Measurements.

The percentage deviations of the measurements of various observers from the results of the present work are shown in Fig. 1. The 4 curves also shown in this figure represent the deviations of values computed by

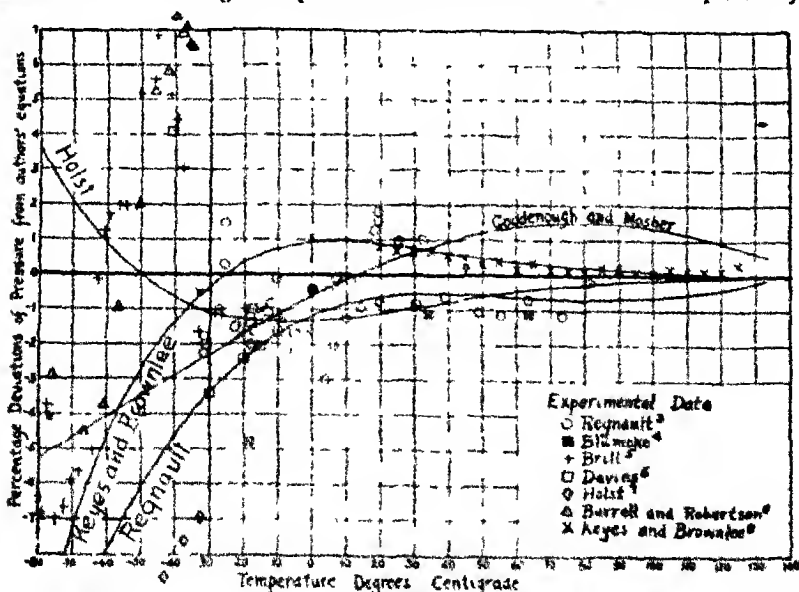


Fig. 1.—Comparison of measurements of the vapor pressure of ammonia.

For references 3, 4, 5, 6, 7, 8, a. see the next column

Regnault, Goodenough and Mosher, Holst, and Keyes and Brownlee. A brief review of the previous measurements may be found in the complete paper.¹

Various determinations of the normal boiling point of ammonia are given in Table I. Several of the earlier determinations were made by immersing a thermometer into liquid ammonia exposed to the air in an open vessel. It is now well known that liquid ammonia under these conditions will cool readily to nearly -40° .

TABLE I
Determinations of the Normal Boiling Point of Ammonia

Observer	Date	Degrees	Remarks
Bunsen(a)	1839	-33.4	Observed -33.7° at 749.3 mm
Lair & Drion(b)	1860	-35.7	In an open vessel
Regnault	1862	37.9	Observed -38.1° at 752 mm in an open vessel
Regnault	1862	-32.6	Calculated from equation
Joannis(c)	1893	-35.3	Probably in an open vessel
Ladenburg(d)		-35.0	
Lange(d)		-33.7	
Dickerson(e)		-33.0	
De Forcrand(f)	1903	-32.5	Vigorous boiling in an open vessel
Gibbs(g)	1905	-33.46	
Brill	1906	33.0	
Davies	1906	-33.5	Interpolated graphically from measurements by static method
Burrell & Robertson	1915	-34.6	
Keyes & Brownlee	1916	-33.22	
Bureau of Standards	1919	-33.35	

(a) *Pogg Ann*, 46, 102 (1839)

(b) *Bull soc chim*, 2, 185 (1860)

(c) *Compt rend*, 115, 822 (1892)

(d) Quoted in "Verflüssigtes Ammoniak als Lösungsmittel," by J. Bronn, Berl

1905

(e) Quoted in "Liquid Air and Liquefaction of Gases," by T. O'Connor Sloan, London, 1900

(f) *Ann chim phys*, [7] 28, 537 (1903)

(g) *THIS JOURNAL*, 27, 858 (1905)

Keyes and Brownlee² have recently published the results of their measurements with an absolute piston gage between 0° and the critical tempe

¹ Bur Standards, *Bull* 16 (to be published shortly)

² *Loc cit*

³ *Mem Inst France*, 26, 596 (1862)

⁴ *Weed Ann*, 34, 18 (1888)

⁵ *Ann. Physik*, [4] 21, 170 (1906)

⁶ *Proc Roy Soc (London)*, 78A, 41 (1906-7)

⁷ *Bull Assoc Intern Froid*, 6, No 51 (1915).

⁸ *THIS JOURNAL*, 37, 2482 (1915).

⁹ *Ibid.*, 40, 25 (1918).

ture of ammonia. A special electrical contact method was employed to increase the sensitivity of the piston gage and to decrease the time necessary in making observations. The constant of the piston gage was determined by direct comparison with a mercury column. A 25-ohm platinum resistance thermometer was used in the temperature measurements. Considerable care was taken in the purification of the ammonia used and the difficulty of removing dissolved gases was particularly emphasized. The ammonia vapor was passed into dry ammonium nitrate which made it possible to keep the ammonia at ordinary temperatures at a moderate pressure. It is stated that dissolved gases could be very completely removed from this ammonium nitrate-ammonia solution. Rather sensitive preliminary tests made at this Bureau indicate that the dissolved gases cannot be removed with sufficient completeness by this method alone. The test used by Keyes and Brownlee for the absence of permanent gases was the complete collapsing of the vapor phase without rise in pressure. This may not be a very sensitive test due to the comparatively large solubility of gases in liquid ammonia. The attainment of equilibrium between the liquid and vapor required considerable time according to their experience. The lag appeared to be increased, it is stated, as the liquid was freed more perfectly from dissolved gases and was more pronounced at low temperatures. In our experience dissolved gases were found to increase greatly the lag in coming to equilibrium as illustrated later in the measurements near the boiling point of a commercial sample which was known to contain air. In the absence of dissolved gases the lags were not excessive in our experiments, except in the measurements at temperatures above about $+25^{\circ}$, which were due to thermal lags in the glass apparatus used.

The normal boiling point of ammonia was measured by Keyes and Brownlee by the static and also the dynamic method. The measurements by the static method were very discordant due to the admitted difficulty in maintaining a constant bath temperature. The results obtained are given in a table reduced to the temperature -33° , which shows variations over a range of 40 mm. A direct determination was then made by the dynamic method, using a Beckman thermometer immersed in the liquid and a small heating coil to produce ebullition. The boiling point was observed to be a function of the heating current, varying from -33.13° with no current to -33.70° with 4 amperes. The most probable value of the normal boiling point by this method was chosen as -33.21° .

The table containing all their experimental data reduced to integral degrees of temperature shows variations in the temperature interval 0° to 50° of about 0.5% in the individual measurements, made at a given temperature. At the higher pressures, the agreement is much better,

which indicates the unsuitability of their piston gage for measurements of low pressures. The deviations of the mean of the observations reduced to integral degrees of temperature are shown in Fig. 1. The curves marked Keyes and Brownlee represent the deviations of values computed by their empirical equation from the present author's equations.

III. General Description of Apparatus and Method.

Manometers.—The manometers used in making the present measurements were of 3 types as shown in Fig. 2. The glass tubes used in each type were of 7 mm. i. d. and 1.5 mm. wall thickness. A calibrated metric scale etched on a strip of silvered plate glass was attached directly behind each manometer.

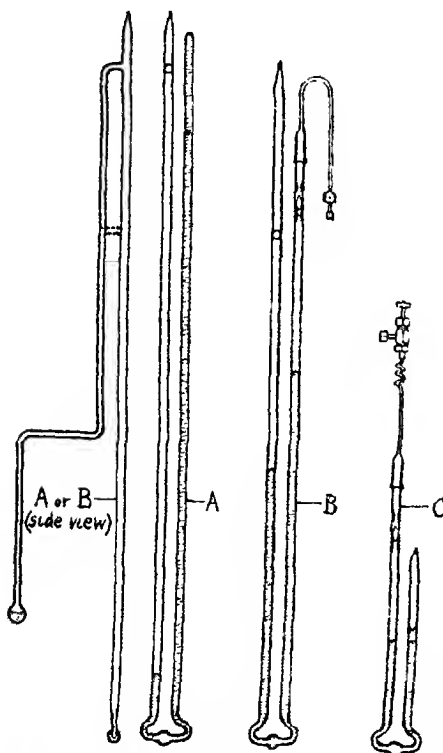


Fig. 2.—Hermetically sealed ammonia containers

scale etched on a strip of silvered plate glass was attached directly behind each manometer.

Type A consists of a glass U-tube containing mercury with one arm evacuated and sealed and the other arm connected to a bulb containing the liquid ammonia. The pressure in this type and also in Type B is transmitted from the liquid ammonia, contained in the small bulb and maintained at constant temperature, to the mercury manometer by means of superheated ammonia vapor. Type A was used in the measurements from -78° to the normal boiling point.

Two manometers of the Type B were used in measuring pressures from slightly below the normal boiling point to that corresponding to $+25^{\circ}$. This type is similar to the former except that one arm is here attached, through a glass-steel joint and a short spiral coil of flexible copper tubing, to a brass needle valve. A small glass float fitting loosely at the bottom and ground at the top is also contained in this arm to act as a check valve to preserve the ammonia in case of a sudden release of the balancing pressure. Measurements near the normal boiling point

were made by opening the brass valve to atmospheric pressure. Manometer and barometer readings were then taken simultaneously. At the higher pressures a balance was obtained by admitting pressure from a cylinder of compressed air, connected by copper tubing to the brass valve. A steel bomb of about 3 liters capacity was inserted in the connecting line and immersed in a large insulated bath of liquid at room temperature to damp out, during any series of measurements, the effect of small change in room temperature on the pressure of this constant volume of air.

Two manometers of Type C were used to measure the higher pressures corresponding to temperatures above room temperature. In this case the liquid ammonia was enclosed in one arm of the manometer and the whole manometer immersed in a thermoregulated bath. Air pressure was used here, as before, to obtain a balance in pressure within a few cm. and manometer readings were taken through a window in the bath.

Pressure Gages.—An open mercury manometer was used to measure balancing pressures from one to fifteen atmospheres. This manometer will be described in detail elsewhere¹ and only a brief description will be given here. It consists of 5 glass U-tubes, each having a length equivalent to 3 atmospheres pressure. By a proper manipulation of valves the U-tubes may be connected in series or by-passed to measure any pressure from one to sixteen atmospheres. The pressure is transmitted between tubes by a liquid of known density, alcohol in the present case. Readings of the mercury levels in the various arms are made upon accurately calibrated metric scales of steel. A specially constructed and calibrated mercury thermometer with a bulb 2.4 meters in length is used to measure the average temperature of the mercury columns.

The piston gage used to measure the higher balancing pressures will also be described in detail elsewhere.² It was designed and constructed to measure pressures up to 100 atmospheres. The pressure measurements were made by weighing the force exerted against a rotating steel piston floating in oil. The piston has an area of about one sq. cm. A small mercury manometer, from which the pressure is transmitted to the piston by means of oil, serves to indicate when the piston is in equilibrium.

Constant Temperature Baths.—The thermoregulated bath used in the measurements below room temperature with manometers of Types A and B has been previously employed in the determination of specific and latent heats of ammonia and described in detail elsewhere.³ It consists of a brass vessel, with two cylindrical vertical tubes connected at the bottom and near the top, filled with gasoline. The smaller tube

¹ Dickinson and Meyers, *Bur. Standards, Bull.* (to be published shortly).

² *Lac. cit.*

³ Osborne, *Bur. Standards, Bull.* 22, 1906, p. 100.

contains a screw propeller, electric heating coil, carbon dioxide cooling coil, and a thermostat coil filled with toluene. An oscillating contact in the thermostat head, previously described,¹ served to maintain the temperature constant to about one thousandth of a degree.

In the measurements above room temperature a large thermoregulated bath of about 100 liters capacity was used. This bath consists of half a wooden barrel filled with water and provided with a stirrer, heating coil, and thermostat. Evaporation to the room provided the necessary cooling and by the use of the oscillating contact in the thermostat head the temperature of the bath could be maintained remarkably constant for long periods of time.

Thermometers.—Platinum resistance thermometers of the 4-lead potential terminal type with strain-free winding previously described by Waidner and Burgess² were used in all the temperature measurements. The wheatstone bridge used in the observations of the platinum thermometer resistances has been previously described.³

IV. Purification of Samples and Description of Manometer Fillings.

The ammonia used in these measurements was prepared by methods to be described in detail in an independent paper. Only a brief description of the process of purification will, therefore, be given here.

A sample of synthetic ammonia (designated Sample K in a previous analysis),⁴ which proved to be extremely pure except for a small amount of water and non-condensing gases, was transferred by distillation into a special small steel container which would hold about a kilogram. The first portion was distilled off and the middle portion distilled into a similar vessel containing a large quantity of metallic sodium, in the form of a fine wire, to remove any remaining traces of water. The ammonia remained in contact with the metallic sodium for about a week. During this interval the liquid was frequently shaken and the hydrogen blown off. The liquid was distilled into a high-pressure distillation apparatus, and fractionally distilled 8 times, rejecting the first and last fractions (about $\frac{1}{10}$ the total volume of liquid) in each distillation. The rejected fractions were removed through a mercury seal in such a way as to discard the non-condensing gas present. After the above treatment, which was all of a preliminary nature, the final product was distilled into a vacuum fractional distillation apparatus of glass and fractionally distilled at least 10 times under widely different conditions of temperature and pressure, the first and last portions being rejected in each case.

Since the accuracy of the physical measurements depends largely upon

¹ Sligh, *THIS JOURNAL*, 42, 60 (1916).

² Bur. Standards, *Bull.* 6, 154 (1910); *See Paper 124*.

³ Mueller, Bur. Standards, *Bull.* 11, 571 (1914); *See Paper 241*.

⁴ McKelvy and Taylor, *J. Am. Soc. Refrig. Eng.*, 3, No. 5, 43 (1917).

the purity of the ammonia used and especially upon having the amount of non-condensing gases reduced to a minimum, particular care was taken in the removal of these gases. The ammonia was, therefore, frozen with liquid air and the vapor then pumped off by means of a high vacuum pump. The ammonia was then allowed to warm up until it was entirely liquid and some of the vapor allowed to escape through the mercury seal. It was again frozen with liquid air and the vapor pumped off as before. This process was repeated several times. Finally the ammonia was frozen into small, flocculent crystals by its own evaporation, the resulting vapor being pumped off and discarded. During this series of operations samples were taken continuously and the amount of non-condensing gas determined by a method previously outlined,¹ to be described more in detail in a later paper.

The tests on the final samples of ammonia, used in filling the vapor pressure manometers, gave the following results: non-condensing gases in the vapor at $+25^{\circ}$ and 760 mm. pressure, less than one part in 100,000 by volume, water, less than 0.003% by weight, which was practically the limit of sensitivity of the chemical test applied.

The vapor pressure manometers were thoroughly cleaned with conc. nitric and sulfuric acids, and aqueous potassium hydroxide solution, and washed with distilled water. They were then sealed, one at a time, into the glass line of the vacuum distillation apparatus. A flask containing about 50 cc. of mercury, purified by the anode process and by distillation, was sealed into the connecting line in such a manner as to permit the mercury to be distilled into the manometers under a high vacuum. In one case, a manometer of Type B was heated to 300° in a specially constructed electric furnace, before filling with mercury, to drive off more completely any occluded gases. (The vapor-pressure measurements made with this manometer, designated B₁ in Table II, show no systematic difference, however, from those made with other manometers which were not given this treatment.) A portion of the purified ammonia was then distilled into each manometer, being frozen in finely divided crystals by means of liquid air. After a sufficient quantity had been distilled into the apparatus, the supply reservoir was cut off by closing an intervening stopcock and the vapor phase pumped off with the aid of a high vacuum pump. The manometers were finally sealed, with the vacuum pump still in operation.

V. Description of Preliminary Experiments.

In the preliminary experiments two phenomena were observed which determined to a large extent the procedure adopted in the final measurements. A brief discussion of them is, therefore, given here.

1. Hysteresis in an Impure Sample.

investigation an attempt was made to determine the boiling point of a commercial sample of ammonia by measurements of the vapor pressure near the normal boiling point, using the static method. The apparatus used in these measurements was similar to Type B (Fig. 2) except that the open end of the manometer tube was drawn down to a small capillary and sealed. When the liquid ammonia in the bulb had been cooled to within a few degrees of the normal boiling point, the glass tip of the capillary was broken off to admit atmospheric pressure. The pressure was then determined from readings of the manometer and the barometer.

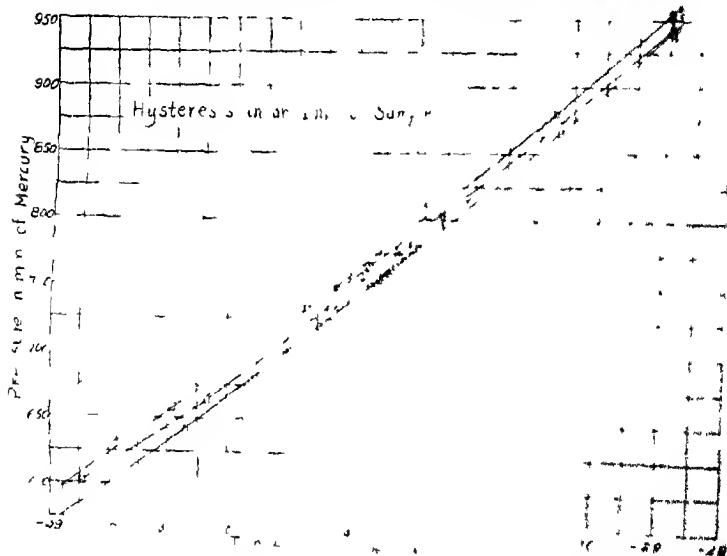
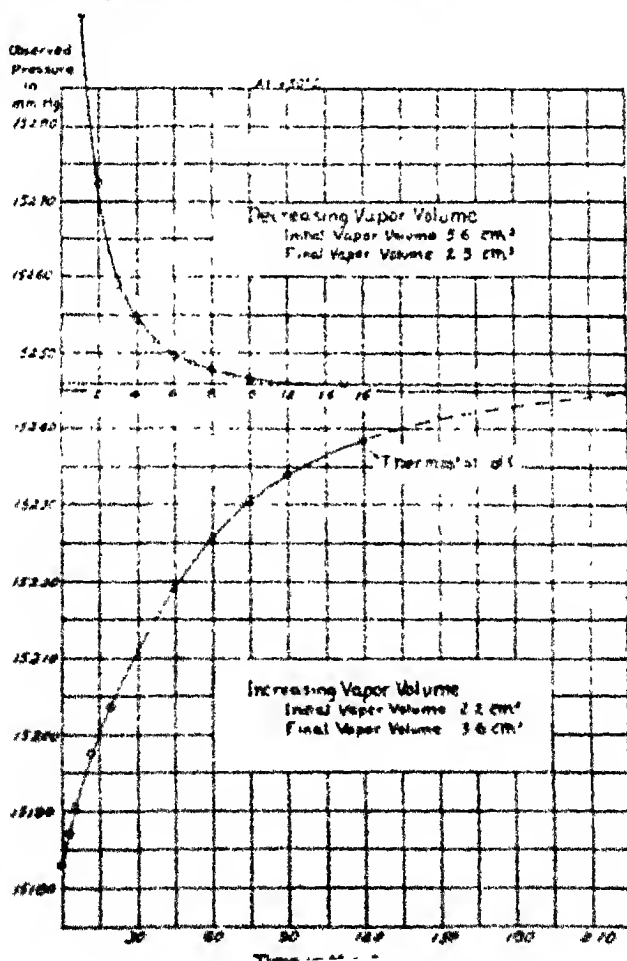


Fig. 3—Comparison of measurement with a pure and impure sample

Fig. 3 illustrates the results obtained with a commercial sample known to contain air as compared with those obtained with a thoroughly purified sample almost completely freed from dissolved gases. The observations taken with the commercial sample are numbered in the order in which they were made. No definite procedure was followed in these measurements to insure equilibrium. Observations were made about 5 or 10 minutes after the regulation of the bath at a constant temperature had been accomplished and consequently do not represent the system in equilibrium. The observations designated 4, 5 and 6 were made at a constant bath temperature, 4 soon after the bath temperature had been raised about 4 degrees, 5 after an interval of one hour, and 6 fifteen minutes later. The lower curve represents the vapor-pressure measurements with a pure sample, taken with a similar apparatus and procedure.

which show no evidence of hysteresis but lie consistently on a smooth curve. The occurrence of hysteresis, at least, with the type of apparatus here used, furnishes an excellent test of the presence of non-condensing gases even in very small quantities.

The phenomenon of hysteresis is undoubtedly associated with the presence of non-condensing gases in the ammonia, but whether the phenomenon observed is due primarily to changes in the amount of gas in solution in the liquid or to changes in the distribution of the gas between the saturated and superheated vapor has not been determined. While the observed pressures were always above those for pure ammonia, the phenomenon produced by the presence of non-condensing gas is evidently much more



complex than the mere increase of pressure by an approximately constant amount.

2. **Lag in Coming to Equilibrium.**—With a purified sample of ammonia well freed from dissolved gases no very great difficulty was encountered at temperatures below 0° in establishing equilibrium conditions, *i. e.*, constant pressure at a constant bath temperature. Non-condensing gases present, however, greatly increased the lag in coming to equilibrium as shown in the previous section. Equilibrium could be obtained at higher temperatures within a comparatively short time only when a certain procedure was followed.

Fig. 4 shows that only a few minutes were required to establish equilibrium when a slightly excessive balancing pressure was used which produced a decrease in the vapor volume and condensation of the vapor. This procedure was finally adopted in all the vapor-pressure measurements. Much greater lags were observed when too small a balancing pressure was used so that the vapor volume was increasing which necessitated evaporation of the liquid. The lower curve shown in this figure was determined by first obtaining equilibrium conditions and then decreasing the balancing pressure a small amount with the bath maintained at a constant temperature. This curve indicates that equilibrium would have been reached only after some hours. A similar phenomenon was observed when the bath temperature was raised and the balancing pressure maintained constant.

Fig. 5 shows qualitatively the variation at different temperatures of

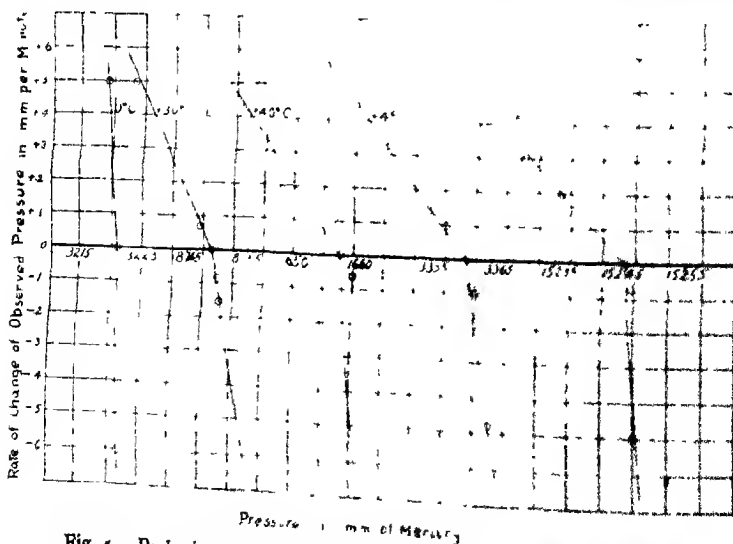


Fig. 5.—Preliminary measurements showing effect of non-equilibrium.

the observed vapor pressure with the rate of change of vapor volume which corresponds in this case with the rate of change of observed total pressure. The lag is evidently much greater with increasing vapor volume or positive rate of change of observed pressure and apparently increases with temperature and vapor density.

A simple calculation of the time required to transmit, through the glass walls, sufficient heat to the surface of the liquid ammonia in order to vaporate the requisite amount of liquid to saturate the increased vapor space indicates that lags of this magnitude are to be expected. This time is obviously greater at the higher temperatures here employed since the vapor density increases very rapidly (for example, it is 5 times as great at $+50^{\circ}$ as at 0°) thus necessitating the evaporation of a greater quantity of liquid and, therefore, a greater amount of heat transfer. The correct order of magnitude of the time required to reach equilibrium upon decreasing the vapor volume may be obtained by a similar calculation. The comparatively large surface available for condensation with this procedure decreases to a great extent the lags in coming to pressure or thermal equilibrium. Doubtless agitation or stirring of the liquid would tend to reduce very materially these lags. With a metal container they would also be reduced due to the larger thermal conductivity of metal as compared with glass.

All of the preliminary measurements, most of which are shown in Fig. 5, have been discarded and no weight given to them in the final result. They were purposely made under very poor conditions to determine the most advantageous procedure to secure equilibrium and also to study the magnitude of the error produced in the pressure measurement.

VI. Measurements by the Static Method.

Measurements below -55° .—Measurements of the vapor pressure were made at 3 temperatures below -55° , the lower limit of the thermostated gasoline bath with carbon dioxide refrigeration. The constant temperatures employed in these measurements were obtained at the freezing point of commercial chloroform, the triple point of ammonia and the temperature of a mixture of solid carbon dioxide and gasoline at atmospheric pressure.

The bulb containing the liquid ammonia of the manometer (Type A) and a platinum resistance thermometer were immersed in a double-walled glass tube, partially filled with commercial chloroform. The glass tube and contents were placed in a bath of gasoline which was cooled by adding solid carbon dioxide. No provision was made to prevent the condensation in the tube of moisture from the atmosphere since only a constant temperature was desired. Stirring of the chloroform was produced mechanically and readings

Several determinations, which will be published later, of the freezing point of pure ammonia under its own vapor pressure (the triple point) have been made in a special apparatus provided with a resistance thermometer and a stirrer operated from the outside by a magnet. Measurements of vapor pressure at this point were made with a small mercury manometer attached to this apparatus and readings taken with a cathetometer. Meniscus corrections were applied to the manometer readings.

The manometer of Type A was used in the vapor-pressure measurements with a carbon dioxide-gasoline slush bath. The temperature of the slush bath was measured in the first experiment with a platinum resistance thermometer and in another experiment with a carbon dioxide vapor-pressure thermometer.

Measurements above -55° . Manometers of Types A and B were used in the measurements from -55° to the normal boiling point of ammonia. Two manometers of Type B were used in the majority of the measurements between the normal boiling point and room temperature. The measurements made with the first filling of these manometers are designated B_1 and B_3 , while those made with the second filling are designated B_2 and B_4 . In each experiment approximate pressure equilibrium was obtained by producing condensation of the vapor and a series of 4 or 5 readings, which served as a test of the equilibrium prevailing during the experiment, was taken to constitute one measurement of the vapor pressure.

In a few experiments 2 manometers (designated B_1, B_2) were used at the same time, that is, with the same bath and the same balancing pressure. The pressures measured on these manometers were identical under these conditions.

Meniscus Depression.—The heights of the menisci in the manometer tubes were not measured consistently throughout these experiments. The heights on the ammonia side of the manometers were observed, however, to be very uniform (about 1.5 mm) while those in the opposite arms were somewhat flatter. Assuming, in the extreme case, one meniscus entirely flat and the other 1.5 mm in height, the maximum error introduced would be about 0.8 mm in the 7 mm tubes used, according to the data of Mendeleeff and Gutkowski.¹ Since the heights in one arm of the manometers were observed to be slightly greater than the other, a uniform correction of -0.3 mm. has been applied to all the observed pressures.

Unit of Pressure.—All of the pressure measurements were reduced to mm. of mercury at 0° and standard gravity ($g = 980.665$).² The value

¹ Landolt and Börnstein, *Tabellen*, 1912, p. 34.

² This value was adopted by the International Committee on Weights and Measures in 1901 (*Travaux et Mémoires du Bur. Int.*, third general conference, 1901, p. 44).

of g in this laboratory is 980.091 based on a direct determination made by the Coast and Geodetic Survey in 1910.¹

Temperature Scale.—The platinum resistance thermometers used in all the temperature measurements were calibrated in ice, steam and sulfur vapor (444.6° taken as the normal boiling point of sulfur). The constants determined by this calibration are:

Thermometer	R_{100}	$R_{100} - R_0$	t
C ₁	25 5440	9 9958	1 491
C ₂	25 5484	9 9876	1 495
C ₃	25 5345	9 9865	1 488

Using the Callendar equation $t = \frac{R_t - R_0}{R_{100} - R_0} 100 + b \left(\frac{t}{100} - 1 \right) \frac{t}{100}$, as an interpolation equation, the temperature scale so defined represents the centigrade thermodynamic scale in the interval -40° to $+450^\circ$ to the accuracy with which that scale is at present known. The scale defined by the resistance thermometer of pure platinum has been adopted as the standard working scale of the Bureau of Standards for use in the interval -40° to $+450^\circ$. Temperatures between 0° and $+100^\circ$ may be measured on this scale with a precision of a few thousandths of a degree. Below -40° temperatures determined by the above equation are consistently lower than those determined with a gas thermometer. By direct comparison of several resistance thermometers of very pure platinum with a constant volume hydrogen thermometer, Henning² found that the following corrections were necessary to reduce to the gas scale the temperatures determined with these thermometers by means of the Callendar equation: $+0.01^\circ$, $+0.06^\circ$, and $+0.16^\circ$ at 220° , 200° and 180° A., respectively. The temperature measurements below -40° C. in this work have accordingly been corrected by interpolation between these corrections.

Results.—The results of all the measurements by the static method, except the preliminary measurements previously referred to as having been rejected, are given in Table II, which gives the date of the experiment, the sample used, the observed temperatures and pressures, and the deviations in mm. of mercury of the observed values from the empirical equations, given in Section IX.

It may be noted from the following table of results that 4 values of the vapor pressure of ammonia may be obtained which are independent of the temperature scale employed. These are at the temperature of (1) the melting point of ice; (2) the freezing point of pure mercury; (3) the triple point of ammonia; and (4) the normal sublimation point of carbon dioxide. The corresponding vapor pressures of ammonia observed at these

¹ Bur. Standards, B. N. S. 10, 1910.

TABLE II
Measurements of Vapor Pressure of Ammonia by the Static Method.

Date	Sample	Obs temp deg	Pres. obs. by manometer mm mercury	Deviations from equi- librium mm mercury	Date	Sample	Obs temp deg	Obs pres by manometer mm mercury	Deviations from equilibrium mm mercury
June 25, '19	A	-78.44	42.2	-0.6	May 10, '19	B ₄	-25.019	1136.6	+0.4
June 25, '19	A	-78.45	42.8	+0.1	Apr 15, '19	B ₂	-25.018	1136.3	0.0
July 26, '19	Special	-77.70	44.9	-0.4	Apr 16, '19	B ₂	-25.005	1137.0	+0.1
June 26, '19	A	-64.50	121.2	0.0	Mar 15, '19	B ₁	-22.812	1257.3	+0.1
June 25, '19	A	-64.27	122.8	-0.3	Mar 15, '19	B ₁	-22.782	1259.2	+0.1
Mar 14, '19	B ₁	-53.036	256.3	+0.9	May 6, '19	B ₄	-20.012	1426.3	+0.2
Nov 22, '18	A	-51.760	276.6	+0.7	May 7, '19	B ₂	-20.008	1426.9	+0.6
Nov. 30, '18	A	-51.603	278.9	+0.3					
Mar 15, '19	B ₁	-50.717	294.5	+0.7	Apr 16, '19	B ₂	-20.005	1426.6	+0.1
Mar 18, '19	B ₂	-50.717	294.4	+0.6	Apr 15, '19	B ₂	-20.004	1426.2	-0.4
Mar 14, '19	B ₁	-48.495	335.2	+0.3	May 2, '19	B ₄	-20.002	1427.3	+0.6
Nov 30, '18	A	-48.172	341.9	+0.6	May 7, '19	B ₂	-15.046	1769.8	+0.8
Nov 22, '18	A	-47.781	349.5	+0.4	Apr 10, '19	B ₂	-15.025	1770.9	+0.3
Nov 26, '18	A	-47.620	352.3	-0.1	Apr 17, '19	B ₂	-15.020	1770.9	0.0
Nov 30, '18	A	-45.946	388.3	+0.5	May 6, '19	B ₄	-15.003	1772.5	+0.3
Nov 22, '18	A	-44.597	419.0	+0.5	May 6, '19	B ₄	-15.002	1772.6	+0.6
Nov 22, '18	A	-44.270	426.2	0.0	May 7, '19	B ₂	-10.024	2179.8	+0.2
Nov 14, '19	A	-44.169	428.6	0.0	May 7, '19	B ₂	-10.020	2179.8	+0.9
Mar 14, '19	B ₁	-44.059	431.9	+0.7	Nov 2, '19	B ₄	-10.010	2181.4	+0.1
Mar 15, '19	B ₁	-44.034	432.4	+0.6	Apr 16, '19	B ₂	-10.009	2180.7	+0.1
Mar 18, '19	B ₂	-43.937	434.3	+0.1	Apr 15, '19	B ₂	-9.990	2180.5	-0.9
Nov 30, '18	A	-43.423	436.9	+0.1	Apr 16, '19	B ₂	-9.990	2180.5	-0.9
Nov 26, '18	A	-42.476	471.2	+0.5	May 3, '19	B ₂	-5.061	2654.1	+0.4
Nov 23, '18	A	-40.274	530.6	+0.2	May 3, '19	B ₂	-5.021	2659.8	+0.4
Nov 22, '18	A	-40.240	531.8	+0.5	Apr 17, '19	B ₂	-5.016	2659.7	-0.2
Mar. 14, '19	B ₁	-38.875	572.0	+0.5	May 6, '19	B ₄	-5.014	2660.2	+0.1
Nov. 30, '18	A	-38.873	571.6	0.0	May 7, '19	B ₂	-5.010	2660.3	-0.2
Dec. 3, '18	A	-38.873	571.3	-0.3	Apr 17, '19	B ₂	-5.003	2661.7	+0.7
Dec. 3, '18	A	-38.873	571.9	+0.3	Apr 15, '19	B ₂	0.000	3220.7	-0.3
Dec. 2, '18	A	-38.872	571.7	+0.1	Apr 16, '19	B ₂	0.000	3220.8	0.0
Nov. 30, '18	A	-38.872	571.8	+0.2	Apr 17, '19	B ₂	0.000	3220.7	-0.1
Nov. 28, '18	A	-38.872	571.7	+0.1	May 3, '19	B ₄	0.000	3220.4	-0.4
Nov. 28, '18	A	-38.872	571.6	0.0	May 6, '19	B ₄	0.000	3221.2	+0.4
Nov. 29, '18	A	-38.872	571.7	+0.1	May 7, '19	B ₄	0.000	3220.8	0.0
Nov. 29, '18	A	-38.872	571.9	+0.2	May 7, '19	B ₄	0.000	3221.2	+0.4
Nov. 29, '18	A	-38.870	571.9	+0.2	May 14, '19	B ₄	+5.022	3871.5	+0.4

Mar. 13, '19	B ₁	—38.867	572.0	+0.2	May 13, '19	B ₁	3.022	3870.3	—0.8
Nov. 29, '18	A	—38.866	571.7	+0.1	May 16, '19	B ₁ B ₂	4.974	3864.3	—0.1
Mar. 15, '19	B ₁	—38.865	572.1	+0.3	May 16, '19	B ₁ B ₂	9.994	4610.9	—0.3
Mar. 17, '19	A	—38.861	571.8	—0.1	May 15, '19	B ₁	10.021	4615.4	—0.1
Nov. 20, '18	A	—37.643	610.2	+0.4	May 14, '19	B ₁	10.035	4618.3	+0.6
Nov. 20, '18	A	—36.781	637.9	+0.1	May 16, '19	B ₁ B ₂	15.008	5463.3	—0.5
Nov. 22, '18	A	—36.667	641.2	—0.4	May 15, '19	B ₁	13.159	5491.3	0.0
Nov. 22, '18	A	—36.645	642.5	+0.2	May 16, '19	B ₁	20.018	5492.3	+0.2
Mar. 28, '19	C ₁	—36.616	643.6	+0.3	May 16, '19	B ₁ B ₂	20.020	6432.3	—0.5
					May 15, '19	B ₁	25.016	7525.1	+0.8
					May 17, '19	B ₁ B ₂	25.176	7561.9	+0.4
Dec. 2, '18	A	—36.605	643.5	—0.2					
Nov. 30, '18	A	—35.476	682.5	+0.2					
Nov. 26, '18	A	—34.907	702.8	+0.4					
Nov. 26, '18	A	—34.119	731.1	+0.1					
Nov. 30, '18	A	—33.746	745.1	+0.2					
Nov. 23, '18	A	—33.389	758.7	+0.3					
May 2, '19	B ₁	—33.369	760.2	+0.1	Mar. 22, '19	C ₁	15.120	5485.5	+1.5
Apr. 15, '19	B ₁	—33.368	759.3	+0.1	Mar. 26, '19	C ₁	24.951	6427.4	—1.0
May 5, '19	B ₁	—33.363	760.1	+0.7	Mar. 26, '19	C ₁	25.081	7515.1	—1.2
Apr. 17, '19	B ₁	—33.361	760.0	+0.5	May 19, '19	C ₁	29.916	7538.4	—0.7
Mar. 28, '19	C ₁	—33.361	760.1	+0.6	Apr. 1, '19	C ₁	30.002	8735.0	+3.5
Mar. 28, '19	C ₁	—33.354	760.1	+0.4	Apr. 1, '19	C ₁	30.058	8749.8	+0.2
Mar. 18, '19	B ₁	—33.314	761.6	+0.3	May 20, '19	C ₁	35.022	10137.0	—4.4
Nov. 22, '18	A	—33.305	761.2	—0.4	May 23, '19	C ₁	35.022	10133.3	+2.5
Nov. 22, '18	A	—33.297	761.3	—0.6	May 23, '19	C ₁	39.928	11037.8	+3.0
Nov. 22, '18	A	—33.283	762.2	—0.3	May 26, '19	C ₁	39.928	11636.6	+1.8
Nov. 22, '18	A	—33.270	763.4	+0.4	May 26, '19	C ₁	30.005	11661.5	+5.0
Nov. 15, '19	B ₁	—33.257	763.4	—0.1	Mar. 31, '19	C ₁	44.919	13332.7	+0.5
Nov. 30, '18	A	—33.244	763.6	—0.4	Apr. 2, '19	C ₁	44.965	13348.7	0.0
Dec. 3, '18	A	—33.243	764.3	+0.3	May 20, '19	C ₁	45.071	13368.9	+2.3
Mar. 17, '19	A	—33.241	764.3	+0.4	May 23, '19	C ₁	50.016	15262.3	+2.6
Mar. 14, '19	B ₁	—33.123	768.9	+0.3	Mar. 31, '19	C ₁	50.083	15274.1	—4.2
Mar. 14, '19	B ₁	—30.451	877.4	+0.4	May 20, '19	C ₁	50.117	15293.0	+1.2
Apr. 16, '19	C ₁	—30.081	893.3	—0.7	May 26, '19	C ₁	55.004	17327.0	+2.1
May 2, '19	B ₁	—30.038	895.8	+0.8	May 27, '19	C ₁	60.057	19632.1	—1.5
May 10, '19	B ₁	—30.011	897.1	+0.9	May 27, '19	C ₁	60.062	19635.6	—0.4
Apr. 17, '19	B ₁	—30.004	896.9	+0.4	May 27, '19	C ₁	60.062	19630.1	+3.1
Apr. 16, '19	B ₁	—29.913	900.7	+0.2	May 27, '19	C ₁	60.060	19632.4	+2.7
Mar. 18, '19	B ₁	—25.059	1134.7	+0.1	May 27, '19	C ₁	60.066	19638.1	+0.2
Mar. 18, '19	B ₁	—25.030	1134.7	+0.1	May 27, '19	C ₁	65.051	22136.7	+1.6
May 2, '19	B ₁	—25.035	1136.0	+0.6	May 27, '19	C ₁	65.059	22139.6	+0.3
					May 27, '19	C ₁	65.063	22140.1	—1.2
					May 28, '19	C ₁	70.011	24843.5	—4.6
					May 28, '19	C ₁	70.011	24842.6	—5.5

Pres. obs. by
piston gauge
mm. mercury

temperatures are (1) 3220.8 mm., the mean of 7 experiments; (2) 571.8 mm., the mean of 14 experiments in which the bulb containing ammonia was immersed in freezing mercury; (3) 44.9 mm., the mean of 2 experiments with the 3 phases solid, liquid, and vapor present; and (4) 42.2 mm., the mean of 2 experiments with sub-cooled liquid ammonia.

The mean of the seventeen observations taken within 0.1° of the normal boiling point of ammonia with 6 different samples and corrected to 760 mm. pressure gives the value -33.354° .

VII. Determination of the Normal Boiling Point by the Dynamic Method.

In order to check the measurements of the normal boiling point of ammonia by the static method, a direct determination was undertaken by the dynamic method, analogous to the ordinary method of measuring steam points.

The apparatus used consisted of 2 concentric tubes of pyrex glass cemented together to form a double walled vessel as shown in Fig. 6.

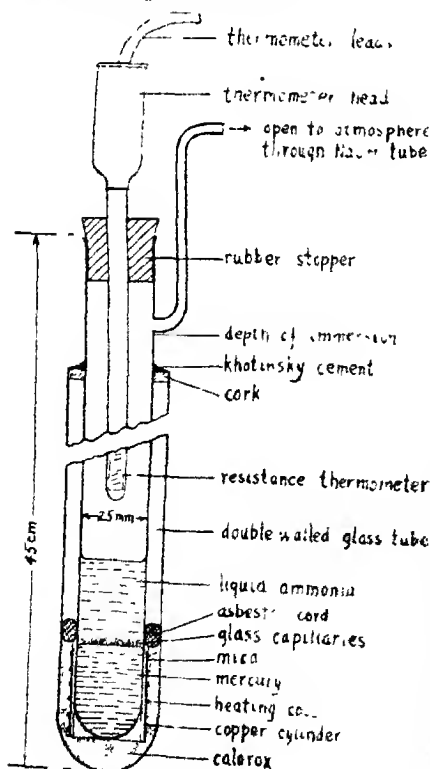


Fig. 6.—Boiling point apparatus

About 20 cc. of pure mercury and a large number of small glass capillaries were placed in the bottom of the inner tube to promote uniform boiling. A rubber stopper in the open end served to hold the platinum resistance thermometer in place and allowed it to be moved up and down. After a thorough cleaning the apparatus was placed in a thermostated bath, evacuated and cooled below the normal boiling point of ammonia. Commercial ammonia of high purity contained in a small cylinder was then distilled into the apparatus through sodium hydroxide in a drying tube. Chemical tests made upon this commercial sample indicated less than 0.01% of solid impurities (residue on evaporation) 0.01% volatile carbon compounds and 0.03% of water.

TABLE III.

Determination of the Normal Boiling Point by the Dynamic Method.

Date.	Bath temp degrees	Heating current Amp	Height of therm above liquid in cm	Depth of liquid in cm	Bar Rdg reduced to 0° & sp gr	Temps obs	Normal boiling point
Aug 15, '19. ...	-48	1 0	10	5	749 87	-33 589	-33 322(a)
	-48	1 0	10	5	749 87	-33 602	-33 335(a)
	-48	1 0	10	5	749 82	-33 612	-33 343(a)
	-48	1 0	10	5	749 82	-33 615	-33 346(a)
Aug. 19, '19 ..	-40	1 0	7	4	750 65	-33 593	-33 346
	-40	1 0	3	4	750 60	-33 594	-33 345
	-40	1 0	11	4	750 55	-33 594	-33 344
	-40	1 0	15	4	750 50	-33 594	-33 343
	-40	1 0	2	9	750 27	-33 583	-33 327
	-40	1 0	10	9	750 27	-33 583	-33 327
	-40	1 0	therm immersed:		750 20	-33 541	-33 283(b)
	-40	1 0	5	9	750 14	-33 595	-33 335
	-38	0 9	5	9	750 08	-33 614	-33 352
	-38	0 9	10	9	750 06	-33 612	-33 350
	-42	1 1	10	9	750 08	-33 610	-33 348
	-42	1 1	10	9	750 08	-33 611	-33 349
	-49	1 1	10	9	750 39	-33 592	-33 339
	-49	1 1	5	9	750 39	-33 594	-33 341

Mean = -33 341

(a) Very irregular boiling—observations taken without the addition of mercury.

(b) Not included in mean.

The results of observations which were taken under various experimental conditions, are shown in Table III. The thermometer was placed at different heights above the boiling liquid as the test of a sufficiently high condensation line to produce uniform temperature. In one instance the bulb of the resistance thermometer was completely immersed in the boiling liquid and a rise in temperature of about 0.05° was observed. The mean of 17 observations corrected to temperatures corresponding to 760 mm. pressure gives the value -33.341° for the normal boiling point.

VIII. Form of Empirical Equations.

Numerous empirical equations of widely different forms have been proposed in the past century to represent vapor pressures as a function of temperature. Attempts have been made to establish this functional relationship upon a semi-rational basis by introducing approximations into the Clapeyron equation and then integrating. The Rankine-Dupré formula

$$\log p = A + B/\theta + C \log \theta$$

sults for a large number of substances with a fair degree of approximation. Similarly Nernst deduced an equation of the form

$$\log p = A + B/\theta + C \log \theta + D\theta$$

which represents very accurately pressure measurements within a limited region, particularly in the region below the normal boiling point. Quite recently Brunelli¹ has gone one step farther and proposed an empirical equation of the form

$$\log p = A + B/\theta + C \log \theta + D\theta + E\theta^2 \quad (1)$$

He has evaluated the constants in this equation for water and compared the calculated values of vapor pressure with those determined by experiment which are more accurately known perhaps than for any other substance. The agreement throughout the range from 0° to the critical temperature is remarkably good. A similar empirical equation of the form

$$\log p = A + B\theta + C\theta + D\theta^2 + E\theta^3 \quad (2)$$

has been used by Keyes and Brownlee to represent their experimental results on ammonia.

Equations of the form (1) and (2) were found to represent very closely the results of the present experimental work and also Cardoso and Giltay's² determination of the critical data. An equation of the form

$$\log p = A + B/\theta + C/\theta^2 + D/\theta^3$$

was tried but did not represent the data satisfactorily.

IX. Discussion of Results.

The results of the measurements may be expressed equally well by means of either of the following empirical equations

$$\log_{10} p = 30.256818 - \frac{1914.9569}{\theta} - 8.4598324 \log_{10} \theta + 2.39309 \times 10^{-3} \theta + 2.955214 \times 10^{-6} \theta^2$$

and

$$\log_{10} p = 12.465400 - \frac{1648.6068}{\theta} - 0.01638646 \theta + 2.403276 \times 10^{-3} \theta^2 - 1.168708 \times 10^{-6} \theta^3$$

which were made to agree with Cardoso and Giltay's critical data, $p_c = 85348$ mm. and $\theta_c = 132.9^\circ$. In these equations p and θ are expressed in mm. of mercury and degrees absolute, respectively ($^\circ \text{ abs.} = ^\circ \text{ C.} + 273.1$).

The deviations of the individual measurements in mm. of mercury from values computed by these equations are shown in Table II. In the 122 measurements made with the single manometers and the open

¹ *Nuovo Cimento*, 14, 57 (1917).

² *Arch. sci. phys. nat. Genève*, 34, 20 (1912).

mercury manometer in the interval from -78° to $+25^{\circ}$, inclusive, the maximum deviation is 1.1 mm. and the average deviation is 0.3 mm., which is within the limit of error of actual pressure observation. In the 28 measurements made in the interval $+15^{\circ}$ to $+70^{\circ}$, inclusive, with the piston gage, the maximum deviation is 5.5 mm., at the highest temperature, and the average deviation is 2.1 mm. or on the average about 2 parts in 10,000 in the pressure. This agreement is very satisfactory when consideration is given to the precision of the piston gage and also to the effect of temperature on the pressure, for example, an error of 0.01° in the temperature is equivalent in this range to from 2 to 6 mm. in the pressure.

The majority of the measurements except those below the normal boiling point were purposely taken at approximately 5° intervals, within 0.1° . The rate of change of vapor pressure with temperatures computed from the above equations was used to correct the individual measurements to the integral degrees. The means of these corrected measurements are given in Table IV and compared with the calculated values. The deviations, expressed in degrees C. indicate the good agreement between observed and calculated values.

TABLE IV.
Deviations of Mean Observed Pressures from Authors' Equations in Degrees.

t	No. of obs.	Mean P_{calc}	t_{calc}	t_{calc} in 0.001°	t	No. of obs.	Mean P_{calc}	t_{calc}	t_{calc} in 0.001°
-78.0	3	44.00	-78.076	-76	$+3$	3	3867.9	$+4.999$	$+1$
-64.0	2	125.29	-64.016	$+16$	10	3	4612.2	10.000	0
-51.0	4	289.43	-50.966	-34	15	3	5462.6	14.999	$+1$
-48.0	4	345.03	-47.983	-17	20	3	6428.2	19.998	$+2$
-44.0	7	432.98	-43.987	13	25	4	7520.5	25.000	0
-40.0	2	538.58	-39.990	10	30	2	8750.9	30.007	-7
-38.870	14	571.77	-38.867	-3	35	2	10123.5	35.003	$+3$
-33.354	17	760.00	-33.347	-7	40	3	11661.4	40.010	-10
-30.0	6	897.2	-29.989	-11	45	3	13362.3	45.003	-3
-25.0	6	1137.4	-24.995	-5	50	3	15245.4	50.000	0
-20.0	3	1427.0	-19.997	-3	55	1	17325.3	55.005	-3
-15.0	5	1772.8	-14.995	-5	60	5	19606.1	59.999	$+1$
-10.0	5	2181.6	-9.998	-2	65	3	22108.5	65.000	0
-5.0	6	2661.5	-5.000	0	70	2	24836.8	69.991	$+9$
0	8	3226.8	0.000	0					

The remarkable reproducibility of the observed pressures at the normal boiling point and at the ice point (0°) on different days and with various samples seems to preclude the possibility of any systematic error due to the sample, which was not obscured by errors of measurement or, in other words, that the material was of a high degree of purity. The agreement between the pressures observed at the

indicates that no appreciable systematic error resulted from the use of the latter. Additional confirmation of this is furnished in the careful calibration of the piston gage against the open mercury manometer.

The slope of the vapor-pressure temperature curve for ammonia is expressed equally well by the differentiation of either of the above equations as follows:

$$\frac{dp}{d\theta} = 2.30258 \frac{p}{\theta} \left(\frac{1914.9569}{\theta} - 8.4598324 \log_{10} \theta - 2.39309 \times 10^{-4} \theta + 5.910428 \times 10^{-8} \theta^2 \right)$$

and

$$\frac{dp}{d\theta} = 2.30258 \frac{p}{\theta} \left(\frac{1648.6068}{\theta} - 0.01638646 \theta + 4.806552 \times 10^{-5} \theta^2 - 3.506124 \times 10^{-8} \theta^3 \right)$$

where $dp/d\theta$ and p are in mm. of mercury and θ in degrees absolute, ($^{\circ}\text{abs.} = ^{\circ}\text{C.} + 273.1$).

The estimated errors in the values of $dp/d\theta$ thus obtained are, from consideration of Table IV, about one part in 200 in the range -80° to -50° , one part in 500 in the range -50° to -30° and one part in 1000 in the range -30° to $+70^{\circ}$.

The results of the measurements of the normal boiling point by the static method, which give a mean value of -33.354° , are in fair agreement with the measurements by the dynamic method whose mean is -33.341° . The normal boiling point of ammonia is, therefore, taken as -33.35° .

The present work has been carried out with very pure samples of ammonia. The question immediately arises in the practical application of the results as to how much the results would be affected by the impurities commonly found in commercial samples. The normal boiling point found by the dynamic method in which the temperature of the condensing vapor is measured, would be very little affected by these impurities while a satisfactory determination by the static method with commercial samples is practically impossible. This illustrates the fact that the results obtained in measurements with impure materials may depend more upon the method chosen than upon the purity and that refined physical measurements should be attempted only with the purest materials. The impurities present in commercial materials may prevent the engineers being able to utilize fully the accuracy of the physical data, yet the data for pure material are at least as likely to be representative of a given commercial sample as data on impure material. As shown in the normal boiling point determinations, the properties of commercial samples under proper conditions may differ very slightly from those of a pure material.

In conclusion, the authors wish to acknowledge their indebtedness to Dr. C. W. Waidner, E. F. Mueller and E. C. McKelvy, of this Bureau, for many valuable suggestions during the progress of this investigation.

X. Summary.

A detailed description is given of the apparatus and method employed in the present measurements throughout the temperature interval -78° to $+70^{\circ}$.

Seven samples of thoroughly purified ammonia were used. Special tests showed less than one part in 100,000 by volume of non-condensing gases present, and less than 0.01% by weight of other impurities. The methods of purification and filling of manometers are briefly described.

The phenomenon of hysteresis was observed near the normal boiling point of ammonia with a commercial sample containing a small amount of air, which indicated the necessity of very complete removal of dissolved gases for any accurate measurements of vapor pressure by the static method. Lags in coming to equilibrium were encountered and studied in order to determine the most advantageous procedure in establishing equilibrium.

The normal boiling point of ammonia was determined by the static and also the dynamic method, the mean of the results by the two methods being -33.35° .

Two empirical equations were found to represent closely the results in the temperature range covered experimentally and also the latest determination of the critical data for ammonia. The results of 122 measurements in the interval -78° to $+25^{\circ}$ made with direct observations of mercury columns agree with the empirical equations within one mm. of mercury. The results of 28 measurements in the interval $+15^{\circ}$ to $+70^{\circ}$ made with an accurately calibrated piston gage agree with the empirical equations within about 3 mm. of mercury.

As a final result the vapor pressure of ammonia is expressed in the range -80° to $+70^{\circ}$ by either of the following equations:

$$\log_{10} p = 30.256818 - \frac{1914.9569}{\theta} - 8.4598324 \log_{10} \theta + 2.39309 \times 10^{-3} \theta + 2.955214 \times 10^{-5} \theta^2$$

$$\log_{10} p = 12.465400 - \frac{1648.6068}{\theta} - 0.01638646 \theta + 2.403276 \times 10^{-3} \theta^2 - 1.168708 \times 10^{-5} \theta^3$$

where p is expressed in mm. of mercury and θ in degrees absolute, ($^{\circ}$ abs. = $^{\circ}$ C. + 273.1). The slope of the vapor pressure curve is

APPENDIX I.

Degrees C.	0	1.	2	3.	4	5	6	7	8.	9.
Vapor Pressure of Ammonia (mm Mercury at 0° and $g = 980.665$).										
-80	37.6									
-70	81.9	76.1	70.6	65.5	60.6	56.1	51.9	48.0	44.3	40.8
-60	164.2	153.7	143.7	134.3	125.4	117.1	109.2	101.8	94.7	88.1
-50	306.6	288.8	272.0	255.9	240.7	226.2	212.5	199.4	187.0	175.3
-40	538.3	510.1	483.1	457.3	432.7	409.1	386.6	365.2	344.7	325.2
-30	896.7	853.9	812.8	773.3	735.4	699.0	664.1	630.6	598.5	567.8
-20	1426.8	1364.6	1304.6	1246.8	1191.0	1137.2	1085.3	1035.4	987.4	941.2
-10	2181.4	2094.2	2009.7	1928.0	1848.9	1772.4	1698.5	1627.0	1557.9	1491.2
0	3221.0	3102.2	2987.0	2875.2	2766.7	2661.5	2559.4	2460.4	2364.5	2271.5
+0	3221.0	3343.0	3468.5	3598.0	3731.0	3868.0	4009.0	4153.5	4302.5	4455.0
10	4612.0	4773.5	4939.0	5109.0	5283.5	5462.5	5646.0	5834.5	6027.5	6225.5
20	6428.5	6636.5	6849.5	7068.0	7291.5	7520.5	7755.0	7995.0	8240.5	8492.0
30	8749.0	9012.0	9281.0	9556.0	9837.0	10124.0	10418.0	10718.0	11025.0	11338.0
40	11658.0	11985.0	12318.0	12659.0	13006.0	13361.0	13723.0	14092.0	14469.0	14853.0
50	15245.0	15645.0	16052.0	16467.0	16891.0	17323.0	17763.0	18211.0	18667.0	19132.0
60	19606.0	20089.0	20580.0	21080.0	21589.0	22108.0	22636.0	23173.0	23720.0	24276.0
70	24842.0									

Atmospheres (1 atmos = 760 mm Mercury)

Degrees C.	0	1.	2.	3	4	5	6	7	8	9.
-80	0.0495									
-70	0.1078	0.1001	0.0929	0.0861	0.0797	0.0735	0.0674	0.0613	0.0552	0.0493
-60	0.2161	0.2022	0.1891	0.1767	0.1651	0.1541	0.1437	0.1339	0.1246	0.1159
-50	0.4034	0.3800	0.3578	0.3367	0.3167	0.2977	0.2796	0.2624	0.2461	0.2307
-40	0.7083	0.6712	0.6357	0.6017	0.5693	0.5383	0.5087	0.4805	0.4536	0.4279
-30	1.1799	1.1236	1.0695	1.0175	0.9676	0.9197	0.8738	0.8297	0.7875	0.7471
-20	1.8774	1.7956	1.7166	1.6405	1.5671	1.4963	1.4281	1.3624	1.2992	1.2384
-10	2.8703	2.7555	2.6443	2.5368	2.4328	2.3322	2.2349	2.1406	2.0499	1.9621
0	4.2380	4.0818	3.9303	3.7832	3.6405	3.5020	3.3677	3.2375	3.1112	2.9888
+0	4.2380	4.3985	4.5640	4.7340	4.9090	5.0895	5.2750	5.4655	5.6610	5.8620
10	6.0685	6.2805	6.4985	6.7225	6.9520	7.1875	7.4290	7.6770	7.9310	8.1915
20	8.4585	8.7320	9.0125	9.3000	9.5940	9.8955	10.2040	10.5195	10.8430	11.1735
30	11.512	11.858	12.212	12.574	12.943	13.321	13.708	14.103	14.507	14.919
40	15.339	15.770	16.209	16.656	17.113	17.580	18.056	18.542	19.038	19.543
50	20.059	20.585	21.121	21.667	22.224	22.793	23.372	23.962	24.562	25.174
60	25.797	26.432	27.079	27.737	28.407	29.089	29.784	30.491	31.211	31.943
70	32.687									

APPENDIX II.

Rate of Change of Vapor Pressure with Temperature ($dp/d\theta$) mm Mercury per Degree.

Degrees C.	0	1.	2.	3	4	5	6	7	8	9.
-80	3.08									
-70	6.02	5.66	5.31	4.98	4.66	4.36	4.08	3.81	3.55	3.31
-60	10.81	10.23	9.67	9.14	8.63	8.14	7.67	7.22	6.80	6.40
-50	18.15	17.28	16.44	15.63	14.85	14.10	13.38	12.70	12.05	11.42
-40	28.82	27.58	26.38	25.22	24.10	23.02	21.98	20.97	20.00	19.06
-30	43.61	41.92	40.28	38.69	37.15	35.65	34.20	32.79	31.42	30.10
-20	63.29	61.08	58.93	56.83	54.78	52.78	50.84	48.95	47.12	45.34
-10	88.64	85.83	83.08	80.40	77.78	75.21	72.70	70.26	67.88	65.56
0	120.35	116.90	113.49	110.14	106.86	103.66	100.53	97.46	94.45	91.51

APPENDIX II (continued).

Degrees C.	0.	1	2.	3.	4.	5.	6.	7	8.	9
+ 0	120 35	123 90	127.55	131 25	135 00	138 80	142.70	146 70	150 75	154.90
10	159 10	163 40	167 75	172 20	176 70	181 30	186 00	190 75	195 45	200.50
20	205 50	210 55	215 70	220 95	226 30	231 70	237 20	242 80	248.50	254.25
30	260 1	266 0	272 0	278 1	284 3	290 6	297 0	303 5	310.0	316.6
40	323 3	330 1	337 0	344 0	351.1	358 3	365 6	373 0	380 5	388.1
50	395 8	403.6	411 4	419 4	427 5	435 7	444 0	452 3	460.8	469 4
60	478.1	486 9	495 8	504 8	513 9	523 1	532 4	541 8	551.3	561 0
70	570 8

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

REPRODUCIBLE LIQUID JUNCTION POTENTIALS: THE FLOWING JUNCTION.¹

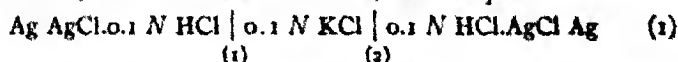
BY ARTHUR B. LAMB AND ALFRED T. LARSON.

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The potentials of liquid junctions in voltaic cells are sources of perplexity in measurements of the electromotive force of cells and of the single potentials of electrodes, not only because they evade direct observation, complete elimination, or a rigorous calculation, but because they are also a frequent source of considerable experimental uncertainty. It has been particularly difficult to secure reproducible liquid junction potentials when the ions on the two sides of the junction have marked differences in mobility. Uncertainties in such junctions frequently amount to several millivolts.²

We have recently been engaged upon a study of the Thomson effect in electrolytes, which involved the precise measurement of the electromotive force of cells containing 2 or more liquid junctions. This has led us to a study of the reproducibility of such junction potentials and ultimately to the development of a type of junction, which, even under unfavorable conditions, that is, with ions of marked differences in mobility, gives electromotive forces reproducible to 0.01 of a millivolt.

In this study we followed 2 procedures: first, we constructed cells similar to those of Chanot³ containing 2 identical but oppositely directed liquid junctions, and 2 identical electrodes, for example:



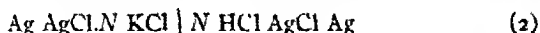
Such a cell should give a constant zero potential. If it does not, and the

¹ This investigation was completed in December, 1915; an account of it was presented before the Harvard-Technology Physical-Chemical Club in February, 1916.

² Chanot, *Ann. Univ. Lyon, Nouv. Ser.*, 1, 1906, 18; Cumming, *Trans. Faraday Soc.*, 9, 174 (1913); Lewis, Brighton and Sebastian.

electrodes are known to be identical and constant, the observed effect must be due to differences and inconstancies in the liquid junctions.

Second, we constructed cells containing constant and reproducible electrodes of the second type, connected by a single liquid junction, as follows:



Such a cell should have a definite and constant electromotive force, whose magnitude will depend, first, on differences in the single potentials of the electrodes in the different solutions, and, secondly, on the potential of the liquid junction itself

The first method is, perhaps, more convenient than the second, in that identical electrodes are used which can be readily checked against each other; on the other hand, it is inferior to the second in the important respect that with *two* junctions the possibility still remains that each junction may be changing at the same rate but in opposite directions, and thus give an apparent but not a real constancy at each junction. For that reason our final experiments have all been carried out by the second method.

The electromotive force measurements were made with a potentiometer reading to one or two millionths of a volt. Elaborate precautions were taken in the matter of screening, and the cells were kept in an oil thermostat at $25^{\circ} \pm 0.01^{\circ}$.

Since the reproducibility of the electrodes was a matter of primary importance in this investigation, electrodes of several different kinds were prepared and studied. The hydrogen electrode was found to be almost ideally reproducible and very convenient, but the slight fluctuations of the electrolyte, caused by the bubbling of the hydrogen gas, produced serious disturbing effects on the liquid junctions.

The calomel electrode was also studied, but after repeated trials was discarded as less permanently reliable than a silver chloride electrode prepared essentially according to the method described by Lewis¹ and by Jones and Hartman,² but with the difference that we deposited the silver chloride in the sunlight and kept the supply solution of hydrochloric acid and potassium chloride, containing silver chloride in suspension, also in the sunlight. This exposure of all the silver chloride to sunlight seemed to bring it into a final condition of equilibrium, for electrodes thus prepared were found to adjust themselves almost immediately after immersion to their definitive potentials, and after standing short-circuited overnight were found to be constant and identical to 0.01 of a millivolt.

Junctions between Ground Glass Surfaces.—In view of the favorable

¹ Lewis, *THIS JOURNAL*, 28, 166 (1906).

² Jones and Hartman, *Ibid.*, 37, 356 (1915).

results obtained by Jones and Hartman¹ we first studied the behavior of liquid junctions formed between the bearing surfaces of ground glass stoppers. For this purpose the above-mentioned cell (No. 1) was assembled as in Fig. 1. Each end of the siphon tube containing the potassium chloride solution was provided with a coarsely ground glass stopper. The

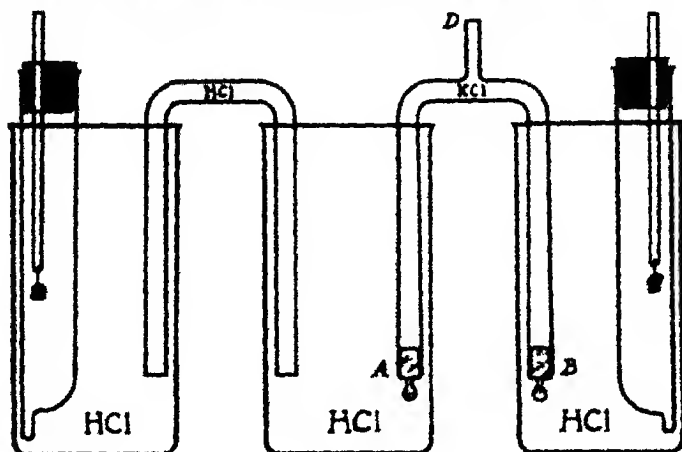


Fig. 1

solution was poured in and allowed to creep well along the bearing surfaces before the siphon was closed at D and placed in position connecting the 2 beakers. The following are typical readings obtained for the potential of the cell which, since the electrodes have been shown to be identical, should be zero.

TABLE I
Junctions between Ground Glass Surfaces.

Time	Millivolt
11 50 A.M.	+0.09
12.15 P.M.	-0.28
2:30 P.M.	-0.22

In general, the e. m. f. varied ± 0.25 millivolt. While such a junction might be suitable in cases where the abutting ions differ but slightly in mobility, it was by no means satisfactory for our purposes.

Diaphragm Junctions.—The glass stoppers were removed from the above siphon and pieces of cotton gauze were stretched tightly over each open end. These ends were then dipped in hot gelatin, which on cooling gave a thin but mechanically strong diaphragm. Using the same potassium chloride solution in the siphon, the following typical results were obtained; they were even less satisfactory than the preceding ones.

TABLE II.
Gelatin Diaphragm Junctions.

Time.	Millivolt. +
1:00 P.M.	0.12
3:00 P.M.	0.14
6:00 P.M.	0.22
10:00 A.M.	0.39
12:00 M. ¹	0.34
1:30 P.M.	0.43

Inasmuch as slight differences and irregularities in the permeability of the gelatin might be responsible for the variable e. m. f., the gelatin-cotton diaphragms were replaced by more permeable ones of parchment paper. Provision for a steady flow of electrolyte was also made by attaching a small separatory funnel containing potassium chloride solution to the upper opening of the siphon D and arranging a small propeller-stirrer to operate just underneath each diaphragm. We hoped by this dynamic method to secure constant conditions at the lower surface of the parchment diaphragm. The typical results obtained are given in Table III.

TABLE III
Dynamic Parchment-Diaphragm Junctions

Time.	Millivolt
4:20 P.M.	+0.08
4:25 P.M.	-0.25
4:50 P.M.	-0.13
5:15 P.M.	+0.14

The variations here, although somewhat less in extent than before, were very sudden and erratic. It developed that they were largely due to irregularities in stirring. Thus, by stopping one stirrer the potential became 0.08 millivolt more positive, stopping the other propeller produced an equal change in the opposite direction. This indicated that a properly controlled dynamic junction offered decided possibilities. It seemed desirable, however, to attempt to secure a similar result by simpler means.

Fresh Junctions.—Influenced by the favorable results obtained by the dynamic compared with the static junction, we studied the effect of forming a fresh junction in an open tube. Following the conclusions of Cumming that reproducible junctions can be secured in this way only in tubes of at least 4 mm. bore, the siphon shown in Fig. 2 (but without the median stopcock) was constructed. C and D were glass tubes of a uniform bore of 5 mm. A fresh junction was established by running out about one cc. of solution from each funnel, whereupon the potential reading was made as rapidly as possible. Typical results secured in this way are given in Table IV.

TABLE IV.
Fresh Junctions.

Time		Millivolt.
9:45	Fresh junction	-0.01
10:00		-0.31
10:05	Fresh junction.	-0.03
11:00		-0.40
11:05	Fresh junction	-0.00
11:15		+0.04
11:25		-0.41
11:27	Fresh junction.	-0.02
11:48		-0.35
11:49	Fresh junction	+0.01

In each case the establishment of a fresh junction brought the liquid junction potential down substantially to zero.

It seemed possible that the wide divergence in potential which these junctions developed on standing, that is, the pronounced "ageing" effect, might be caused by the disturbing oscillations of the liquid in the siphon tube. To eliminate this a glass stopcock was inserted in the median connecting arm. This was kept always closed, but as it was not lubricated, the film of electrolyte between the ground glass surfaces furnished sufficient conductance for our measurements. This arrangement gave very satisfactory results, as shown in Table V. In these experiments, even in the absence of liquid junctions, the e. m. f. would not be zero, as one electrode was, for reasons, connected with our study of Thomson effects, maintained at zero instead of 25° . The extra middle beaker shown in Fig. 1 was necessary under these conditions. The hydrochloric acid solution was 0.09 *N*, the potassium chloride 0.1 *N*.

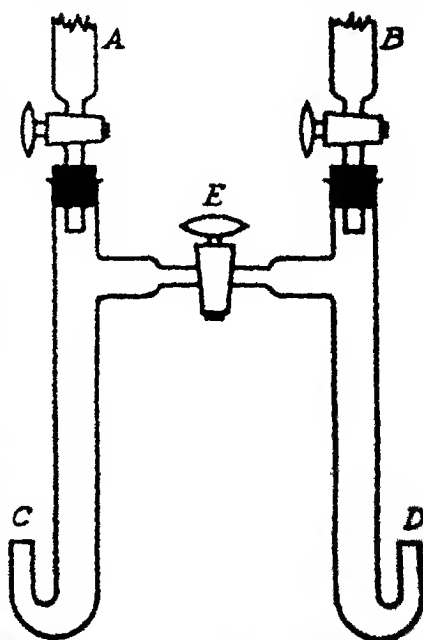


Fig. 2.

These results confirm the great reproducibility of fresh junctions, and also show that where oscillations are prevented very slight

TABLE V.
Fresh Junctions. Closed Tube 0.1 *N* Solutions.

Time.		Millivolts +
2:28	Fresh junction	8.31
2:49		8.36
2:50	Fresh junction	8.32
3:45		8.30
6:30	Fresh junction	8.32

This reproducibility, however, quite vanishes when instead of 0.1 *N*, normal solutions are employed. Thus, with all the other arrangements as before, but using *N* instead of 0.1 *N* solutions, the following typical results were obtained:

TABLE VI.
Fresh Junctions. Closed Tube, *N* Solutions.

Time.		Millivolts +
3:37	Fresh junction	7.37
3:39	Fresh junction	7.62
3:40	Fresh junction	7.45

Here rapid variations of ± 0.3 millivolt were constantly occurring.

Flowing Junctions.—We now tried feeding the electrolyte slowly but continuously from the separatory funnels into the two arms of the siphon, the stopcock, as before, remaining closed. The results, using *N* solutions, were as follows:

TABLE VII.
Flowing Junctions.

Time		Millivolt +
4:05	Flowing	7.85
4:20	Flowing	7.85
4:40	Flowing	7.83
7:13	Flowing	7.81

These results show that even with *N* solutions containing ions as different in mobility as those of potassium and hydrogen, very closely reproducible potentials can be secured by the simple device of a flowing junction.

To confirm this and, if possible, to understand the phenomenon better, we now applied the same technique to the second type of cell described above (2). This was accomplished by placing 2 silver chloride electrodes of the form shown in Fig. 1, one immersed in *N* hydrochloric acid, the other in *N* potassium chloride, in a large beaker containing *N* potassium chloride. The electrode vessel containing the hydrochloric acid was provided with a separatory funnel to allow a slow flow of electrolyte from the electrode vessel into the beaker. With such a cell containing but a single liquid junction, any change which might have cancelled out with the 2 symmetrical junctions of the first type of cell would be ~~there~~

closed. Typical results obtained with this arrangement are given in Table VIII.

TABLE VIII.
Flowing Single Junctions.

Time		Millivolts +
1:25	Flowing..	32.75
3:00		34.27
3:03	Flowing	32.77
3:49		34.13
3:52	Continuously flowing	32.76
3:57		32.75
4:00		33.13
4:11		33.67
4:22		33.73
4:27		33.89
4:29	Flowing	32.75

These results confirm the constancy and reproducibility of the flowing junction. They also disclose the marked ageing effect which occurs with these solutions.

Effect of Stirring.—Cumming¹ states that he was able to secure reproducible results by establishing a fresh boundary and then stirring it. We attempted to test this point, and to compare the potential thus secured with that given by a flowing junction, by alternately establishing a flowing junction, then interrupting the flow and stirring the electrolyte in the mouth of the exit tube with a small glass rod. The following results were obtained (Table IX):

TABLE IX
Comparison of Stirred and Flowing Junctions.

Junction	Millivolts +
Flowing . .	30.29
Stirred ..	30.54
Flowing . .	30.30
Stirred.. .	30.56
Flowing... .	30.30
Stirred.....	30.52
Flowing.....	30.30

The⁹ potential of the stirred junctions was fairly constant but quite different from the very constant value for the flowing junction.

Again, the effects of stirring and of forming the flowing junction in quite a different way were studied with the same electrode and solution as used above, but so arranged that the liquid junction was formed at the meeting point of two streams, one of hydrochloric acid and the other of potassium chloride solution in a glass tube. The arrangement of tubes and funnels for this purpose is shown in Fig. 2.

chloride) was fed upward from the bottom and the mixed liquids passed out the horizontal exit tube B. It will be noted that the tube was constricted at the point A, where the 2 streams met. This was designed to eliminate any dead space and to produce a rapid flow at this point. The constant level attachment at B was found to be quite essential; if

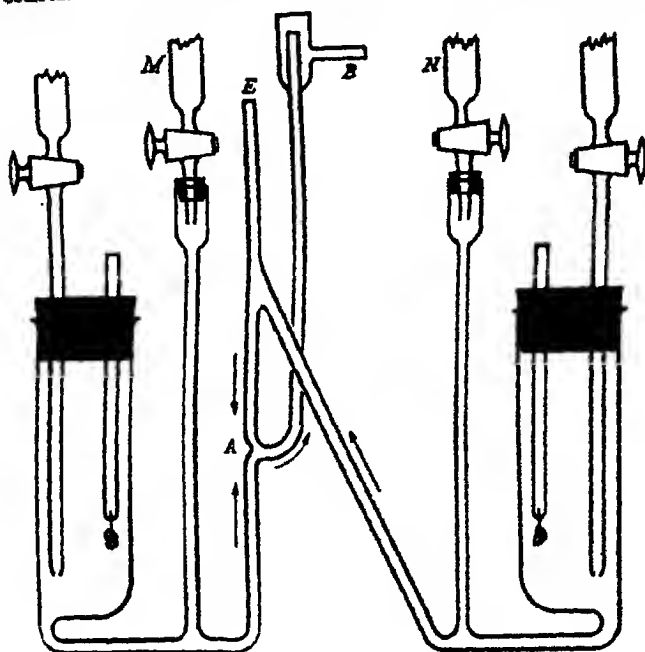


Fig. 3

it were omitted, and the mixed liquid siphoned off, the slight pumping action which resulted was sufficient to disturb the boundary. A long glass rod was also fitted into the tube E by means of rubber tubing, so that by pushing it down and up the junction of A could be stirred. Some typical results obtained with this arrangement are given in Table X.

TABLE X.
Comparison of Stirred and Two-way Flowing Junctions.

Date.	Junction.	Millivolts +
Mar. 3.....	Flowing	30.30
Mar. 4.....	Flowing	30.28
Mar. 4.....	Stirred	30.04
Mar. 4.....	Flowing	30.30
Mar. 6.....	Flowing	30.29
Mar. 6.....	Stirred	30.20
Mar. 6.....	Flowing	30.30

These results show that the liquid junction formed by the confluence of the 2 streams gives exactly the same and just as constant a potential as does the one-way flow of a single electrolyte. However, the stirred junctions formed here were not constant and in general gave lower potentials than the flowing junctions, whereas in the previous arrangement higher results were obtained.

Summary.

The above experiments have shown:

1. That liquid junctions formed between the bearing surfaces of ground glass stoppers, in gelatin diaphragms and in parchment paper diaphragms, with 0.1 *N* hydrogen chloride and potassium chloride solutions are not constant and reproducible to closer than 0.2 or 0.4 of a millivolt.
2. That parchment diaphragms with stirring give somewhat more constant results.
3. That fresh junctions in tubes of 5 mm. bore give potentials reproducible in 0.1 *N* solutions to about ± 0.03 – 0.06 millivolt when oscillations of the electrolyte are prevented, but that with *N* solutions variations of ± 0.3 millivolt occur.
4. That stirred junctions sometimes give very constant potentials, but these are quite different from that produced by a "flowing" junction and, moreover, they differ, depending on the mode of stirring, etc.
5. That a "flowing" junction, obtained simply by having an upward current of the heavier electrolyte meet a downward current of the lighter electrolyte in a vertical tube at its point of union with a horizontal outflow tube, or by allowing the lighter electrolyte to flow constantly into a large volume of the heavier electrolyte, even with *N* solutions, gives potentials constant and reproducible to ± 0.01 of a millivolt.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA.]

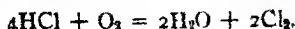
THE REACTION BETWEEN HYDROCHLORIC ACID AND POTASSIUM PERMANGANATE.

By F. P. VENABLE AND D. H. JACKSON.

Received November 24, 1919

On account of its convenience and ease of regulation, the reaction between hydrochloric acid and potassium permanganate has become the usual one for the preparation of chlorine for laboratory purposes. On looking over the text-books one finds some confusion of thought, some misstatements, and a certain amount of evasion of the facts involved. The equation given for this reaction in most of the text-books is

In others it is represented as an oxidation of the hydrochloric acid

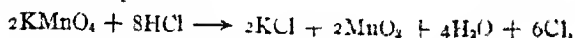


By some the only statement made is that the reactions are quite complicated, and it is also stated that, whether the reaction is between hydrochloric acid and permanganate or manganese dioxide, enough molecules of the acid must be used to furnish hydrogen to combine with all of the oxygen of the oxidizing agent

The following investigation was undertaken to explain certain observations made during the use of this method for class and laboratory purposes, and, if possible, to clear up the confusion in which the matter stands.

When conc. hydrochloric acid is allowed to drop upon solid permanganate chlorine is evolved and a brown black mass is formed. On further careful addition a point is reached where this brown black mass settles out from a colorless liquid and no permanganate is left. This takes place when half the amount of hydrochloric acid called for in the above equation has been added. The brown substance, dried and weighed, is converted quantitatively into Mn_2O_3 by ignition and is, therefore, manganese dioxide.

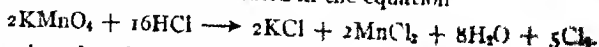
Following these observations quantitative experiments were carried out in which the amounts of permanganate and acid used were those called for in the equation



and the manganese dioxide and chlorine were determined

	I	II	III	I	II	III		
Theoretical, %	MnO ₂	1 10	2 88	2 39,	Cl	1 35	3 53	3 16
Found, %	MnO ₂	1 102	2 85	2 36,	Cl	1 34	3 47	3 18

When the permanganate is used in excess, all over the theoretical amount is left unchanged. When an excess of acid is used the brown-black dioxide is first formed, then dissolved, and so much of the acid enters into the reaction as is indicated in the equation



Changes in color show that there are intermediate reactions. A green solution is obtained under certain conditions indicating the presence of manganese tetrachloride. For the second stage of the reaction application of heat is necessary. This equation was also tested quantitatively, giving the following results

Theoretical, %		I	II	III		I	II	III
Found, %	HCl	4.68	3.69	3.69;	Cl	2.83	2.25	2.25
Found, %	HCl	4.71	3.67	3.66;	Cl	2.81	2.21	2.23

Experiments were then carried out in which dry hydrogen chloride was passed at room temperature over the permanganate placed in a boat in a

glass tube. So long as the permanganate was in excess only the dioxide was formed. The reaction is exothermic and the water formed was vaporized and condensed on the sides of the glass tube. On continuing the passage of the hydrogen chloride after all the permanganate had been acted upon a white crust of manganese chloride and potassium chloride appeared on the dioxide. The presence of the potassium chloride formed before this was doubtless obscured by the dioxide.

It is evident then that there are two reactions taking place in sequence, first, that represented by the equation



and following that, in case excess of acid is used, the reaction



Similar experiments were carried out with potassium permanganate and hydrogen bromide and analogous results obtained. It was noted that hydrobromic acid reacted at a dilution of 0.00154 *N*, whereas no reaction with hydrochloric acid at a dilution beyond 0.002 *N* took place, 50 cc. of the acid being used in each case.

CHAPMAN HILL, N. C.

(CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 118.)

THE IONIZATION AND ACTIVITY OF LARGELY IONIZED SUBSTANCES.¹

BY ARTHUR A. NOYES AND DUNCAN A. MACINNES.

Received November 29, 1919

In applications of the ionic theory of solutions it is customary to employ, in accordance with the original hypothesis of Arrhenius, as a measure of the degree of ionization of salts, acids, and bases, the ratio of the equivalent conductance of the substance at any given concentration to the limiting value of the equivalent conductance as the concentration approaches zero, where the ionization may be assumed to be complete.

This assumption, however, is not a necessary conclusion from the fundamental theory of ionic conduction. According to this theory, the equivalent conductance Λ (which is by definition the quantity of electricity which under a potential difference of one volt passes per second between electrodes of indefinite extent one centimeter apart, between which is placed that quantity of solution which contains one equivalent weight of the ionizing substance) is for a uni-univalent substance given by the expression, $\Lambda = \gamma F(u^+ + u^-)$, in which γ is the fraction of the substance ionized (equal in this case to the number of equivalents of each ion present in the solution) = α .

with each equivalent of ion, and u^+ and v^- the mobilities of the positive and negative ions (that is, their velocities through the solution under a potential-gradient of one volt per cm.) For the equivalent conductance, Λ_0 , at zero concentration, where the ionization becomes complete, we have the corresponding expression $\Lambda_0 = F(u^+ + v^-)$. Combining these two equations we get

$$\frac{\Lambda}{\Lambda_0} = \gamma \frac{1}{u^+ + v^-}$$

From this equation it is evident that Λ/Λ_0 is equal to the ionization only when the mobilities of the ions can be assumed constant up to the concentration under consideration. That they should remain constant so long as the solution does not differ appreciably from water as a viscous medium may seem reasonable, but, in view of possible electrical effects resulting from the large electric charges on the ions, it is by no means certain.

This simple assumption has been justified in the case of slightly ionized acids and bases, where the ion concentration in the solution is small, by the fact that the so-determined ionization values change with the concentration just as the mass-action law requires. This, however, is not true even approximately in the case of salts and of the largely ionized acids and bases (such as hydrochloric acid and sodium hydroxide), and we are forced to conclude, either that owing to the change in the ion mobilities the conductance ratio is not a correct measure of ionization, or that the chemical activity or mass-action effect of ions, and perhaps also of the unionized molecules present with them, is not proportional to their concentration, as the ordinary mass-action law assumes.

In either case the conductance ratio affords no reliable information as to the chemical activity of ions; and we must turn to other properties for a quantitative measure of this important factor, which determines the equilibrium of all chemical reactions between salts, acids, and bases in solution, and also the magnitude of many physical properties thermodynamically related to the activities.

The term activity must in the first place be defined in a precise way; and from a chemical standpoint the most practical method is to define it, as was proposed by G. N. Lewis,¹ as the quantity which when substituted for the concentration of the substance in mass-action expressions, will express its effect in determining the equilibrium. Thus the activity of the substance is its "effective concentration" from this mass-action viewpoint.

Correspondingly, the most obvious method of determining the relative activities of a substance in solutions of different concentrations is to find

¹ Lewis, *Proc. Am. Acad. Arts Sci.*, 43, 239-293 (1907); *Z. physik. Chem.*, 62, 129-165 (1908).

its concentrations in a gaseous phase in equilibrium with the solutions; for in gases at low pressure the concentration and activity can ordinarily be assumed to be proportional. For example, we know that the ratio of the activities of un-ionized hydrochloric acid in its 11-molal and 8-molal aqueous solutions at 30° is 12.0, since the partial vapor pressures of the hydrochloric acid in those solutions have been found to be 11.3 and 0.94 mm. of mercury. This quantity is also the ratio of the products of the activities of the hydrogen ion and chloride ion in the two solutions, since these products are by definition the quantities that must be substituted in the mass-action expression for the equilibrium of the reaction $\text{HCl} = \text{H}^+ + \text{Cl}^-$. Thus denoting the pressures in the two solutions by p_1 and p_2 , the activities of the un-ionized molecules by a_1 and a_2 , and those of the ions by a_1^+ , a_1^- , and a_2^+ , a_2^- , we get

$$\frac{p_1}{p_2} = \frac{a_1}{a_2} = \frac{a_1^+ a_1^-}{a_2^+ a_2^-}$$

This direct method is, however, of very limited applicability in the case of largely ionized substances, since they seldom have appreciable vapor pressures. We have recourse, therefore, to a simple thermodynamic relation between activity and electromotive force. This relation may be derived by considering the work or free-energy decrease attending the transfer of one mol. of the substance (for example, of 1 HCl) from the solution in which its vapor pressure is p_1 to that in which it is p_2 . This free-energy decrease $-\Delta F$ is given by the familiar expression,

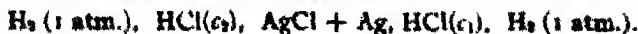
$$-\Delta F = RT \log (p_1/p_2)$$

In this expression, in view of the above considerations, we may substitute for the vapor-pressure ratio the ratio $(a_1^+ a_1^-)/(a_2^+ a_2^-)$ of the product of the activities of the ions, yielding the equation

$$-\Delta F = RT \log \frac{a_1^+ a_1^-}{a_2^+ a_2^-}$$

We thus obtain what may be regarded as a secondary, but more general, definition or measure of activity.

The simplest process from a theoretical standpoint (aside from that already described involving passage through the vapor phase) by which a substance can be transferred from one solution to another is one in which this transfer is brought about in a voltaic cell. Thus in the case of hydrochloric acid, we can cause a transfer of one mol. of the acid from concentration c_1 (activity a_1) to concentration c_2 (activity a_2) by causing one faraday (F coulombs) to pass through the cell.



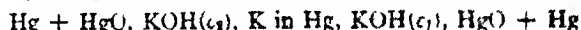
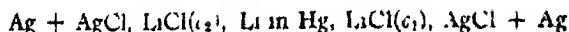
The electromotive force \mathcal{E} of this cell multiplied by the quantity of elec-

state under consideration or the free-energy change attending it. That is,

$$-\Delta F = EF = RT \log \frac{a_1^+ a_1^-}{a_2^+ a_2^-} = RT \log \frac{c_1^+ \alpha_1^+ \alpha_1^-}{c_2^+ \alpha_2^+ \alpha_2^-}.$$

It will be noted that in the last of these expressions there has been written, in place of the activities a of the ions, products αc , in which the quantity α , called the activity coefficient, is evidently the factor by which the total concentration c of the substance must be multiplied to give the activity of the ion.

By the use of this electromotive-force method the authors of this paper have, with the aid of their students, carried out a series of determinations of the activities of typical substances. Two of these researches, those on potassium chloride¹ and on hydrochloric acid,² have already been published; and two more, on lithium chloride and potassium hydroxide, will soon be described in detail in *THIS JOURNAL*. These last investigations were carried out with the aid of grants from the Carnegie Institution of Washington by Mr. J. A. Beattie and Mr. Ming Chow, respectively, using cells, with flowing amalgam electrodes of the following types



It is the purpose of this paper to summarize and compare the results of these investigations and to state the general conclusions to which they lead.

From the observed values of the electromotive forces of these cells there were calculated by the equation given above the products $\alpha^+ \alpha^-$ of the activity coefficients of the 2 ions at various concentrations, the value of the products at the lowest concentration (0.001 to 0.0035 molal) at which accurate measurements could be made being assumed equal to the conductance ratio Λ/Λ_0 at that concentration. These activity-coefficient products were plotted against the logarithms of the concentrations, and those corresponding to round concentrations were read off.

The following table contains the values of the square root of the so obtained products, that is, the values of the expression $(\alpha^+ \alpha^-)^{1/2}$, which represent the geometrical mean of the activity coefficients of the positive and negative ions of the substance. This table also contains the corresponding values of the conductance ratio Λ/Λ_0 , multiplied by the ratio, η/η_0 , of the viscosity of the solution to that of pure water, this last serving to correct approximately for the frictional resistance of the medium to the passage of the ions through it.

¹ MacInnes and Parker, *THIS JOURNAL*, 37, 1443-1461 (1915).

² Ellis *Ibid.* 22, 212-266 (1916).

TABLE I
Activity Coefficients and Conductance-Viscosity Ratios.

Mols per 1000 g of water conc	Activity Coefficients				Conductance-Viscosity Ratios			
	KCl	LiCl	HCl	KOH	KCl	LiCl	HCl	KOH
0.001	0.979	0.976			0.979	0.976	0.990	
0.003	0.943	0.943	0.990	0.982	0.968	0.962	0.986	0.980
0.005	0.923	0.930	0.965	0.975	0.956	0.949	0.981	0.975
0.010	0.890	0.905	0.932	0.961	0.941	0.932	0.972	0.963
0.030	0.823	0.848	0.880	0.920	0.914	0.904	0.957	0.939
0.050	0.790	0.817	0.855	0.891	0.889	0.878	0.944	0.923
0.100	0.745	0.779	0.823	0.846	0.860	0.846	0.925	0.910
0.200	0.700	0.750	0.796	0.793	0.827	0.812	0.909	0.891
0.300	0.673	0.735	0.783	0.769	0.807	0.792	0.903	0.889
0.500	0.638	0.731	0.773	0.765	0.779	0.766	0.890	0.884
0.700	0.618	0.734	0.789	0.772	0.761	0.751	0.874	0.879
1.000	0.593	0.752	0.829	0.786	0.742	0.737	0.845	0.877
2.000			1.040					
3.000		1.164	1.402					

The table contains the results of only the above described researches carried out under our direction. It should be mentioned, however, that exact electromotive-force measurements from which activities can be derived have also been made by Jahn¹ on potassium, sodium, and hydrogen chlorides, by Harned² on potassium chloride; and by Linhart³ on hydrochloric acid. As the results of Harned supplement at higher concentrations those for potassium chloride here presented, it may be stated that, assuming a constant transference number of 0.496 for the potassium ion and an activity coefficient of 0.754 at 0.1 molal as given in the table, his data lead to the following values

Normal concentration.	0.2	0.3	0.5	0.7	1.0	2.0	3.0
Activity coefficient	0.688	0.657	0.624	0.608	0.593	0.572	0.586

The results presented in the table may be summarized as follows:

1. In the case of all 4 substances the activity coefficient decreases with increasing concentration much more rapidly than does the conductance-viscosity ratio, the differences amounting to from 7 to 15% at 0.1 molal, and from 5 to 18% at 0.5 molal.

2. In the case of all the substances except potassium chloride the activity coefficient, unlike the conductance-viscosity ratio, passes through a pronounced minimum in the neighborhood of 0.5 molal, afterwards increasing rapidly at the higher concentrations. Even potassium chloride, according to Harned's data, has a minimum activity coefficient in the neighborhood of 2 *N*.

3. The activity coefficient even at moderate concentrations varies considerably with the nature of the substance; thus its value at 0.5 molal

¹ Jahn, *Z. Physik. Chem.* 111, 1 (1922).

is 55% for potassium chloride, 73% for lithium chloride, and 77% for hydrochloric acid and for potassium hydroxide.

From these facts we may draw the general conclusions that the conductance ratio can no longer be regarded as even an approximate measure of the activity of the ions of largely ionized substances in their mass-action and thermodynamic relations, that this activity varies with the concentration differently in the case of different substances, and that for the present it can only be determined empirically for each substance, with the aid of measurements of chemical equilibrium, electromotive force, or freezing point.¹

It is, moreover, evident that the activity coefficient of the ion constituents cannot be proportional to and mainly determined by the fraction of the substance ionized, for this fraction could not increase with increasing concentration unless the ionizing power of the medium becomes much greater at moderate concentrations, and even then it could not become greater than unity, as is actually the case with the activity coefficient of hydrochloric acid above 2 molal.

The results here presented do not show whether or not the conductance ratio is equal to the degree of ionization. But these two quantities can hardly be equal in view of the fact that the conductances of the two ion constituents of most uni-univalent substances seem to vary by different percentage amounts with increasing concentration, as may be seen from Noyes and Falk's² summary of the experimentally determined transference numbers. These numbers which are equal to the ratio $u^+/(u^+ + u^-)$ of the mobility of the cation constituent to the sum of the mobilities of the two ion-constituents, show variations that correspond to changes in the ratio $u^+ : u^-$ of the mobilities of the 2 ion constituents between zero concentration and 0.3 *N* of 4.5%, in the case of sodium chloride, 7.5% in the case of hydrochloric acid, and 24%, in the case of lithium chloride. Moreover, MacInnes³ has shown that the chloride ion constituent has the same equivalent conductance in 0.1 *N* solutions of lithium chloride, potassium chloride, and hydrochloric acid, although the conductance ratios Λ/Λ_0 for these substances are 0.833, 0.862, and 0.925; so that, if we account for the constancy of the chloride ion conductance by the probable assumptions that the 3 substances are equally ionized and that the chloride ion has the same mobility in the 3 solutions, we must conclude that the hydrogen ion and lithium ion decrease in mobilities between zero concentration and 0.1 *N* by amounts that differ from each other by 10%, a result that makes it not unreasonable to suppose that the whole decrease in equivalent conductance (of 7.5 and 16.5% in the 2

¹ Lewis, *THIS JOURNAL*, 34, 1635 (1912), Bates, *Ibid.*, 37, 1421-1445 (1913).

² Noyes and Falk, *Ibid.*, 33, 1434 (1911).

³ MacInnes *Ibid.* 31, 1026 (1910).

cases) may be due entirely to decrease in mobility of the ions, and not at all to decrease in ionization.

When, indeed, in addition to these conclusions that neither the activity coefficients nor the conductance ratio is determined primarily by the degree of ionization, we take into consideration the fact that there is no property which affords any direct evidence of the existence of un-ionized molecules in solutions of most of the largely ionized inorganic substances up to moderate concentrations, it seems advisable to adopt for the present the hypothesis that such substances are completely ionized, and to attribute the decrease in the conductance ratio wholly to decrease of ion mobility, and the change in activity coefficient entirely to some unknown effect of a physical nature.

It would lead far beyond the scope of this paper to discuss the many classes of phenomena that seem to substantiate this assumption. A summarized description of them was given many years ago by one of the authors of this paper,¹ who at that time, however, suggested that they might be explained more fully by the hypothesis that the ions are partially united, as a result solely of their electrical attraction, into loosely bound molecules, which differ fundamentally from the stable molecules formed as a results of chemical affinity in accordance with the law of mass-action. The known facts may, however, prove to be better accounted for by the simple hypothesis of complete ionization, supplemented by some other, purely physical, explanation of the cause of the decrease of ion mobility and of ion activity with increasing concentration, and this now seems the most promising method of treatment, as has recently been urged by various authors.² As said above, we cannot here discuss in detail the hypothesis of complete ionization, but in closing it may be pointed out that it accounts for the remarkable facts that so many very dissimilar chemical substances (for example, hydrochloric acid and potassium chloride) seem to be equally ionized, and that a volatile substance like hydrochloric acid does not have an appreciable vapor pressure even in *N* solution where 15% of it must be assumed to be in the un-ionized state, if the conductance ratio is taken as a measure of ionization. It may also be mentioned that it avoids the improbable conclusions as to the abnormal activity of the un-ionized molecules to which solubility effects interpreted under the older assumptions lead.³

CAMBRIDGE, MASS.

¹ Noyes, "The Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory," *Congress Arts Sci., St. Louis Exposition*, 4, 317 (1904); *Science*, 20, 382 (1904); abstract, *Z. physik. Chem.*, 52, 635. Also Noyes, *THIS JOURNAL*, 30, 333-333 (1908).

² Milner, *Phil. Mag.*, 35, 214, 334 (1918); Ghosh, *J. Chem. Soc.*, 1918, 420, 627.

(CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 119.)

THE EQUILIBRIUM CONDITIONS OF THE REACTION BETWEEN SILVER SULFIDE AND HYDROGEN.

By F. G. KEYES AND W. A. FELSING

Received November 29 1919

CONTENTS—1 Purpose of the Investigation 2 The Apparatus 3 Preparation of the Materials 4 The Method of Determining the Equilibrium. 5 The Experimental Results 6 Values of the Equilibrium Constant Reduced to Uniform Temperatures 7 Increase in Heat Content Attending the Reaction and Expression of the Equilibrium Constants as a Temperature Function

1. Purpose of the Investigation.

The equilibrium of the reaction $\text{Ag}_2\text{S} + \text{H}_2 = 2\text{Ag} + \text{H}_2\text{S}$ has already been studied by Pelabon¹ at 360 and at 700°. In connection with the systematic investigation of the free energy of formation of the halides, oxides, and sulfides of the elements, mercury, silver, lead, copper, and bismuth, now being carried out in this laboratory, it seemed, however, desirable to make a new series of equilibrium measurements with the view of securing more accurate results than was possible by Pelabon's procedure, and of obtaining reliable values at temperatures far enough apart to enable the heat effect attending the reaction to be calculated by the van't Hoff equation. We have, therefore, carried out a series of determinations in 3 temperature regions having average temperatures of about 750°, 811° and 890° A.

2. The Apparatus.

The apparatus employed was the same in principle as that used by Keyes² in his study of the dissociation pressures of sodium and potassium hydrides. It is shown in Fig. 1. The reaction tube *f* was made of quartz, and was connected by means of a quartz capillary and ground joint to a glass capillary. Hydrogen was prepared in *C* and stored in the reservoir *B*. The whole system could be evacuated by means of the mercury pump *D*, and the analyses of the gaseous phase were made in the water-jacketed gas burets *E* and *F*. The differences in the mercury levels in determining the pressure-volume relations of the gases were read by means of a cathetometer. The furnace used was the same as that used by Keyes. In order to provide a uniform temperature throughout the furnace, the air was vigorously stirred by a fan placed at the bottom of the furnace. The temperature of the furnace was measured by means of a platinum resistance thermometer sensitive to 0.01°.

3. Preparation of the Materials.

The silver sulfide was prepared by precipitating it from silver nitrate solution with hydrogen sulfide. The precipitate was washed by decanta-

¹ *Compt. rend.*, 126, 1864 (1898)

² *This Journal*, 24, 333 (1901)

tion with hot distilled water, collected on a filter, washed, and dried. In order to remove any mechanically adhering sulfur, the finely powdered silver sulfide was heated at 500° in a current of nitrogen.

The hydrogen was prepared by the method used by Keyes; namely, by adding water, free from air and carbon dioxide, to a 5% sodium amalgam.

The hydrogen sulfide was prepared in an apparatus like that used in the preparation of hydrogen by adding a magnesium chloride solution slowly to solid aluminum sulfide. The aluminum sulfide was prepared by heating together lead sulfide and powdered aluminum in a muffle furnace. The magnesium chloride solution was used to prevent the possible introduction of carbon dioxide

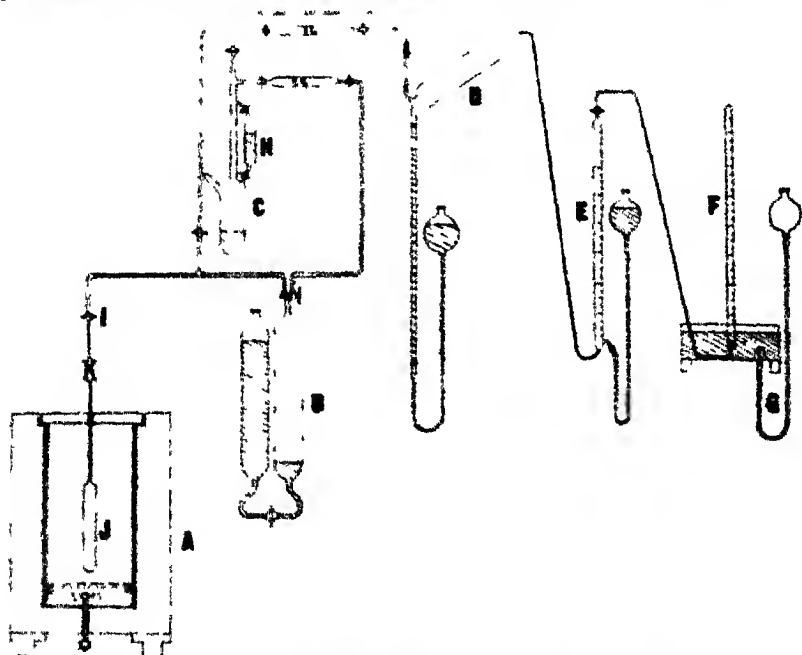


Fig. 1.

Silver in a finely divided state was made by the reduction of an ammoniacal silver nitrate solution by formaldehyde. The precipitated silver was washed repeatedly by decantation, boiled with distilled water, collected on a filter, and dried. It was again dried in a vacuum in the reaction tube at about 450° , thus removing any trace of moisture or of silver oxide.

4. The Method of Determining the Equilibrium.

carbon dioxide in *H*. The apparatus, including the gas reservoir *B*, was thoroughly exhausted by means of the pump *D*. The stop cock at the upper end of the water chamber was opened during the exhaustion for the purpose of removing the last traces of dissolved air and carbon dioxide. A few drops of water were then admitted through the lower stop cock to the amalgam, and the whole apparatus was again exhausted. The water was then admitted to the amalgam, and the evolved hydrogen, dried by passing it slowly through the phosphorus pentoxide tube, was collected in the gas reservoir *F*.

After the reaction tube *I* had been exhausted, a little hydrogen from the reservoir was admitted, and the reaction tube was again exhausted. Hydrogen was then admitted to the reaction tube, which contained the silver sulfide and the stop cock *I* was closed. The temperature of the furnace was adjusted by an outside resistance and the mixture given time to attain equilibrium. Samples of the gas mixture were withdrawn from the reaction tube at different intervals of time, and analyzed to determine whether equilibrium was attained. These time intervals ranged from about 12 hours to a week. The procedure in withdrawing the gas mixture was to exhaust the whole apparatus back of stop cock *I*. The stop cock was then opened, allowing the mixture of gases to rush into the exhausted space and cool instantly. The gases were then transferred to the gas buret *E*, and the volume, pressure and temperature were noted. The gaseous mixture was transferred finally to the gas buret *F*, where the hydrogen sulfide was absorbed by a 23% potassium hydroxide solution, and the residual volume of hydrogen was measured. These measured volumes were reduced to standard conditions of 0° and one atmosphere. In all cases correction was made for the water vapor pressure of the potassium hydroxide solution on the basis of the data given by Bunsen; and the corrections for temperature, height above sea level, and latitude were applied to the observed barometric reading.

Since the partial pressures of the two gases in the equilibrium mixture are proportional to their volume at 0° and one atmosphere, the equilibrium constant for the reaction is given by the expression

$$K = p_{H_2S}/p_{H_2} = v_{H_2S}/v_{H_2}.$$

5. The Experimental Results.

Table I presents the actually observed data, the corresponding volumes of the two gases reduced to the standard conditions of 0° and one atmosphere, and the computed values of the equilibrium constant. The results of Expts. 1 to 19 were obtained by approaching the equilibrium from the hydrogen silver sulfide side; those of Expts. 20 to 22 were obtained by approaching it from the other side.

TABLE I

The Observed Data and the Equilibrium Constants Computed from them

Expt	Equil temp °C	Measurements of gas mixture (H ₂ S + H ₂)			Measurements of gas not absorbed by KOH(H ₂ + H ₂ O)			Vapor pressure KOH at h (H ₂ O)	Calc. volume at 0° and 760 mm. of		Equil constant K = P _{H₂S} /P _{H₂}
		<i>p</i> ₁	<i>p</i> ₂	<i>p</i> ₃	<i>p</i> ₄	<i>p</i> ₅	<i>p</i> ₆		H ₂ (%H ₂)	H ₂ (%H ₂)	
1	478.8	23.20	443.82	23.60	21.80	504.62	15.65	15.80	3.38	9.32	0.3634
2	479.6	24.50	321.45	14.05	24.20	491.08	7.00	18.00	1.45	4.00	0.3631
3	478.8	18.60	371.80	21.00	18.60	508.88	11.60	12.80	2.53	7.09	0.3568
4	468.0	21.40	362.90	19.40	21.80	510.72	10.50	15.20	2.23	6.35	0.3513
5	544.6	26.35	562.72	46.35	26.00	702.33	28.40	19.80	8.01	23.29	0.3440
6	543.3	25.00	548.03	42.40	24.60	688.49	26.95	18.40	6.19	21.81	0.2882
7	540.5	24.20	580.59	45.58	23.75	725.25	28.60	18.55	7.52	24.46	0.3073
8	524.2	22.00	516.39	39.90	22.20	650.68	24.60	16.60	6.09	19.00	0.3205
9	617.2	23.80	520.90	40.20	23.80	687.90	25.25	17.00	5.10	20.48	0.2491
10	616.0	25.12	504.26	39.90	24.60	649.85	23.75	18.40	4.93	18.10	0.2722
11	609.5	23.40	502.96	37.70	22.90	658.59	23.20	16.70	4.96	18.08	0.2745
12	606.1	24.00	493.50	34.60	23.50	647.85	21.40	17.20	4.30	16.35	0.2631
13	629.6	23.20	520.15	18.90	23.40	666.64	24.55	17.20	5.21	19.32	0.2695
14	614.0	24.60	499.70	37.20	23.90	640.91	23.30	17.70	4.87	17.57	0.2771
15	625.0	23.80	541.54	39.85	23.80	691.17	25.15	17.60	5.60	20.50	0.2733
16	633.0	25.80	533.18	40.30	25.20	682.36	25.45	19.00	5.49	20.33	0.2702
17	604.9	22.80	509.65	39.35	23.15	651.48	24.45	16.95	5.49	18.87	0.2909
18	626.4	23.95	516.76	39.50	23.75	680.07	24.60	17.55	5.91	19.73	0.2998
19	616.0	23.01	534.55	38.40	23.15	677.03	23.60	16.95	5.89	18.89	0.3120
20	454.5	25.90	488.78	31.55	26.10	631.01	18.35	19.90	5.06	13.46	0.3761
21	509.9	28.35	538.17	38.45	28.10	678.12	23.90	21.90	5.95	18.71	0.3183
22	557.8	30.08	444.83	24.55	29.15	587.77	14.80	23.15	3.01	9.93	0.3031

6. Values of the Equilibrium Constant Reduced to Uniform Temperatures.

The experiments in which the equilibrium was approached from the hydrogen silver sulfide side are grouped in 3 temperature regions; namely, Expts. 1 to 4 in a region which will be designated Region 1, whose average temperature is 749.15° A., Expts. 5 to 8 in Region 2, whose average temperature is 811.25° A., and Expts. 9 to 19 in Region 3, whose average temperature is 889.63° A. All the separate values of $\log_{10} K$ were plotted against $1/T$, and the best representative line drawn through them. Indeed, it was found possible to draw a single straight line that well represented the points in all 3 regions. To show the concordance of the separate observations, each one was corrected, by taking into account its relation to this line, so as to correspond to one of the 3 average temperatures named above.

The so-reduced values of the equilibrium constant (P_{H_2S}/P_{H_2}), together with their means, are given in the last column of Table II.

TABLE II.
Values of the Equilibrium Constant Reduced to Uniform Temperatures.

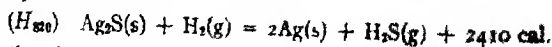
Expt.	Absolute temperature	Equilibrium constant
1	749 15°	0.3652
2		0.3660
3		0.3590
4		0.3450
		Mean, 0.359
5	811 25°	0.3480
6		0.2910
7		0.3310
8		0.3319
		Mean, 0.325
9	889 63	0.2474
10		0.2722
11		0.2711
12		0.2593
13		0.2750
14		0.2763
15		0.2770
16		0.2779
17		0.2850
18		0.3055
19		0.3119
		Mean, 0.278

7. Increase in Heat Content Attending the Reaction and Expression of the Equilibrium Constants as a Temperature Function.

The increase in heat content attending the reaction at the mean temperature (820° A) of the equilibrium measurements may be calculated by substituting the average values of T and K for Regions 3 and 1 given in Table II in the integrated form of the van't Hoff equation, as follows:

$$\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \log_e \frac{K_2}{K_1} - \frac{\Delta H}{1.9885} \left(\frac{1}{749.15} - \frac{1}{889.63} \right) = 2.303 \log_{10} \frac{0.2780}{0.3588}$$

The value of ΔH is thus found to be -2410 cal. This result is expressed by the equation



With the aid of this value we may express the equilibrium constant as a function of the temperature between the limits 750° and 890° A. covered by the experiments. Namely, by substituting in the above given form of the van't Hoff equation the found values of K , T , and ΔH , and writing in place of K_1 and T_1 the general values K and T , we get

$$\log_{10} K = \frac{525.8}{T} - 1.1470$$

The corresponding expression for the free-energy decrease $-\Delta F$ in calories attending the reaction $\text{Ag}_2\text{S} + \text{H}_2 = 2\text{Ag} + \text{H}_2\text{S}$ at any temperature T between 750° and 890°A. is

$$-\Delta F = RT \log_e K = 2408 - 5.253 T.$$

With respect to the concordance of these equations with the observations it may be stated that the first equation, which is derived from the average values of the equilibrium constant at 749.15° and 889.63° , gives for that constant at the intermediate temperature 811.25° the value 0.317, while the average value derived from the observations in that temperature region is 0.325. It may also be mentioned that the results of the 3 experiments (20 to 22 in Table I) in which the equilibrium was approached in the direction opposite to that in which the values on which the equation is based were obtained are in fair agreement with the results computed by the equation, namely, these three experiments gave for the equilibrium constant the values 0.376 at 727.6°A. , 0.318 at 783.0°A. , and 0.303 at 830.9°A. , while those computed from the equation for these temperatures are 0.376, 0.335, and 0.306.

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THE DETERMINATION OF CHLORINE WITH THE NEPHELOMETER.

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In the study of the concentration of the vapor of "mustard gas" and similar non-volatile toxic liquids over areas sprayed with them, large samples of the contaminated air were collected, the toxic gas absorbed therefrom in alcohol, and after special treatment the chlorine was liberated as chloride and determined as such. These "war gases" are so very toxic that extremely minute quantities are significant, and in spite of the large samples of air which were collected (13 liters) it was necessary not only to detect but to measure amounts of chlorine as small as a few thousandths of a milligram.

For the rapid and approximate estimation of these amounts the copper flame test¹ gave useful results, as did also the selenious acid method of Yablick, Perrott and Furman,² but before these methods had been developed, and indeed afterwards when a more quantitative determina-

¹ Published by permission of Maj.-Gen. W. L. Sibert, Director, Chemical Warfare Service, U. S. A.

² Lamb, Carleton, Hughes and Nichols, THIS JOURNAL, 42, 78 (1920).

³ *Ibid.* 42, 266 (1920).

tion was desired, resort was had to the nephelometric method perfected by Richards and Wells.¹

These authors have, however, applied the method only to aqueous solutions, while we were obliged to use an alcoholic solution for the absorption of the toxic gases, and it was desirable if possible to apply the method directly to this solution. Moreover, Wells² in particular, has shown that the development of a maximum opalescence varies greatly with the conditions and that different concentrations require different treatment. Finally, in spite of the great delicacy of this method, the quantities of chloride with which we had to deal were so minute that the method had to be pushed to its utmost refinement.

For these reasons and also to adapt the method to the routine analysis of our many hundreds of samples, a study of it was undertaken, particularly with reference to the development of opalescence, with the result that a number of facts were disclosed which we believe will be of interest to any who may be confronted with analytical problems of this kind.

We first carefully determined the reproducibility of our nephelometric readings. Next, using permanent standards, we studied the development of opalescence and perfected a method for obtaining rapidly a maximum and constant opalescence. We finally studied the effect of diffuse daylight on the opalescence, and very briefly the relative intensities of opalescence of silver chloride suspensions in water, 50% alcohol and 50% acetic acid.

Reproducibility of Nephelometer Readings.

The nephelometers used were of the Kober type.³ The only alteration was to coat the cement on the plungers with a thin layer of paraffin, in order to avoid any contamination of the solution.

Directions for the use of the instruments are given in full by Kober. Our procedure was briefly as follows. At the beginning of a series of analyses both cups of the instrument and both plungers were rinsed first with distilled water and then with the standard suspension (silica or silver chloride) to be used. They were nearly filled with this solution and placed in position in the instrument. The position of the left-hand cup was adjusted until the scale reading was exactly "10.0," the position of the right-hand cup was then adjusted until the illuminations on both sides were equal, this being determined as the average of several independent settings. This setting was retained for the whole series of comparisons with the standard.

¹ Richards, *Proc. Amer. Acad. Arts Sci.*, 29, 74 (1893); Richards and Wells, *Am. Chem. J.*, 31, 235 (1904); Richards and Wells, *THIS JOURNAL*, 27, 485 (1905); Wells, *Am. Chem. J.*, 35, 99 (1906); Richards, *Ibid.*, 35, 510 (1906).

² *Am. Chem. J.*, 35, 99 (1905).
J. Ind. Eng. Chem., 7, 822 (1915).

The solution in the left-hand cup was then discarded, the cup and plunger rinsed with the solution next to be used, and the cup nearly filled with the solution as before. It was placed in position in the instrument and the height adjusted until illuminations on both sides were again equal. The scale reading was recorded and the results computed using the formula given by Kober

$$Y = (20/F) - (1 - F) \times 20 \times (0.052 F^2)$$

Where Y signifies the scale reading, F the concentration, and 0.052 is the nephelometric constant

There are several precautions either not mentioned by Kober, or not sufficiently emphasized, which must be observed if the utmost accuracy in the use of this nephelometer is to be obtained. In the first place, a very serious error may be introduced if the eyepiece of the instrument is not kept in exactly the same position throughout a series of comparisons. Not only does alteration of the position of the eyepiece vary the distribution of light over the field but it changes very considerably the relative positions of the cups for equal illuminations. Thus, in one case, the turning of the eyepiece through 180° caused a change in setting of the left-hand cup from 21.4 to 14.7, the right-hand cup remaining in the same position.¹

Second, a very appreciable error may result from a variation in the light conditions in successive comparisons, unless the position of the cup in its holder is always exactly the same. We found it advisable to mark the cup for this purpose.

Third, the precise matching of two faintly opalescent solutions is difficult. The only practical method of attaining readings of satisfactory accuracy is to raise the left-hand cup until there is a shadow just distinctly visible on the right-hand side of the divided field, then to lower it until a shadow of the same distinctness is visible on the left, and to take the mean of the extreme readings. Moreover, with these faint opalescences satisfactory results can be obtained only when the eyes have acquired their maximum sensitiveness by remaining in the dark for 5 or 10 minutes. Similarly, too long continued observation tires the eyes sufficiently to produce a marked decrease in the accuracy of the settings.

Adopting all the precautions above-mentioned, a series of comparisons of silver chloride suspensions at different concentrations was carried out. The solutions were prepared by adding enough alcohol to appropriate quantities of very dilute standard sodium chloride solutions to bring the volume up to 20 cc., adding 10 cc. of 0.1 *M* nitric acid to this, followed by a large excess (10 cc.) of 0.005 *M* silver nitrate solution, making a total volume of 40 cc. The resulting solutions all at first

proximately 50% alcohol. For preparing the dilute solutions the following standard solutions of sodium chloride were employed:

Final solutions Molar conc. NaCl $\times 10^{-4}$	Initial solutions Molar conc. NaCl
0.37-1.00	0.000100
2.00-4.5	0.000200
9.0	0.000400
18.0-75	0.00200

The reagents had to be purified with care in order to secure reproducible results. Chlorine-free alcohol was secured by the distillation of commercial, 92% alcohol from sodium or potassium hydroxide, using about 2 g. of potassium hydroxide for 700 cc. of alcohol. The water and the nitric acid were also specially redistilled. To eliminate individual differences, the observations were made by 3 different observers. The results obtained are collected in Table I.

TABLE I—REPRODUCIBILITY OF SETTINGS

Molar conc. $\times 10^{-4}$	Total ^a wt. Cl mg.	Observer	Successive settings means of R t and I t			Deviation from average		
			Average			Max	Min	Average
0.37	0.0053	A	10.3	11.6	11.6	11.2	0.9	0.6
0.37	0.0053	B	13.5	12.3	11.4	12.4	1.1	0.7
0.37	0.0053	C	13.1	12.0	12.1	12.4	0.7	0.5
0.50	0.0071	C	14.8	14.6	14.0	14.5	0.5	0.3
1.00	0.0142	C	14.5	14.9	13.4	14.6	0.5	0.2
2.00	0.0284	A	9.7	9.9	10.3	10.0	0.3	0.2
2.00	0.0284	B	9.7	9.7	10.6	10.0	0.6	0.4
4.5	0.064	B	15.1	15.1	15.1	15.1	0.0	0.0
9.0	0.128	A	15.6	15.5	15.8	15.7	0.1	0.1
9.0	0.128	B	15.6	15.3	15.9	15.6	0.3	0.2
18.0	0.256	B	15.8	16.1	16.4	16.2	0.4	0.2
45.0	0.64	B	17.2	17.3	16.9	17.1	0.2	0.2
75.0	1.06	B	18.3	17.6	17.8	17.9	0.4	0.3

^a This refers to the total weight of chlorine in the 40 cc. sample used in the nephelometer.

It is evident from this table that over the range of concentration studied (0.37 — $75 \times 10^{-4} M$) the average deviation is not more than about 2 or 3%. It is also interesting to note that this deviation is least for intermediate opalescences ($5 \times 10^{-4} M$). At these concentrations the settings can be made more rapidly and easily than at higher or lower concentrations. At low concentrations the fields are too faint, and at high concentrations too brilliant for accurate matching. This is confirmed by the average differences between the maximum and minimum settings, as shown, for instance, by the typical results collected in the following table:

TABLE II—DIFFERENCES BETWEEN MAXIMUM AND MINIMUM SETTINGS.

Total wt. Cl. mg.	0.0053	0.0071	0.0142	0.0284	0.064	0.128	0.256	0.64	1.06
Diff.	5.4	4.0	2.0	—	—	—	—	—	—

The average differences are least in the region of intermediate concentrations.

The Development of Opalescence.

Richards and Wells¹ point out that the rate of development of opalescence is decidedly variable in pure water, but by adding a considerable quantity of nitric acid to the solution under comparison, the maximum opalescence is quickly attained by each suspension, and persists unchanged in relative intensity for hours. In all of our solutions we have, therefore, used a very large excess of dil. nitric acid, (10 cc. of 0.1 *M*)

The existence of progressive changes in the state of the precipitate was fully recognized by Richards early in the development of nephelometry, although he did not measure them quantitatively. His method of overcoming uncertainties from this cause was as follows: "The unknown solutions to be estimated must be treated in exactly the same way as the known standard solutions, which serve as the basis of comparison."²

Evidently this method is entirely legitimate and must give accurate results when any reasonable time of standing is allowed.

Wells³ studied the rate of development of opalescence of these solutions in more detail and used fixed standards of ground glass, which showed that the above constancy, while real, was only relative, and that the opalescence after reaching a maximum decreases very slowly in the dilute solutions and very rapidly in the concentrated ones. He recommends that the opalescences of the dilute solutions (0.000,005 *M*) be read within 30 minutes, and of concentrated solutions (0.000,05 *M*) within 4 minutes after precipitation.

It is evident that there are at least 2 effects operative in this phenomenon—one, the progressive increase in the size and number of particles, due to the precipitation of the dissolved silver chloride, another the coalescence of particles so that their net opalescent effect diminishes. In the concentrated solutions, at least, this coalescence progresses so far that visible coagulation occurs. Since precipitation has a steadily decreasing velocity while the coalescence continues indefinitely, there results a period of growth in the intensity of opalescence followed by a usually longer period of decay.

In order to study these questions further, and in particular as applied to our alcoholic solutions, we first prepared a standard of constant opalescence. This was a suspension of kieselguhr made by shaking the finely ground material with distilled water, allowing it to stand for 72 hours and then siphoning off the supernatant liquid. The faintly opalescent

¹ THIS JOURNAL, 27, 485 (1903).

² Theodore W. Richards, "Nephelometry," p. 10.

solution thus obtained was approximately equivalent in the nephelometer to the $4.5 \times 10^{-5} M$ silver chloride standard. The permanence of this suspension was tested by filling the two cups of the nephelometer with the same suspension, and comparing with each other after various time intervals. The left cup and its contents remained undisturbed throughout the series, while the right was emptied, refilled with freshly shaken solution and replaced in the same position before each reading. Typical results were as follows:

TABLE III—PERMANENCE OF KIESELGUHR STANDARD

Time, min	0	5	10	15	20	25	30	40	50	60	70
Reading	15.9	16.0	15.5	15.6	15.5	15.5	15.6	15.6	15.5	15.0	14.6

From these results it is evident that the kieselguhr remained suspended for at least an hour before there was any decided indication of settling, and that if suitable care be taken in replacing the cup in the holder the readings can be closely reproduced. Using this suspension as a standard, measurements of the change of opalescence of the silver chloride suspension with time were made. The silver chloride suspension was prepared as before and was $2.00 \times 10^{-5} M$. It was allowed to stand at 20° for the time intervals indicated in the table, and was then compared with the kieselguhr standard. The opalescences are represented in percentages of that attained after one hour's standing.

TABLE IV—CHANGE OF OPALESCENCE WITH TIME AT 20° Conc. = $2.00 \times 10^{-5} M$

Time of standing, min	7	15	30	45	60	90	120	180
Opalescence, per cent	81	93	98	102	100	102	101	102

A similar suspension of silver chloride was then prepared and heated to 60° for the times indicated, cooled to room temperature and compared with the kieselguhr standard as before. The results are expressed in percentages of the opalescence of the above standard.

TABLE V—CHANGE OF OPALESCENCE WITH TIME AT 60° Conc. = $2.00 \times 10^{-5} M$

Time of heating, min	3	10	25	40	60
Opalescence, per cent	84	112	120	120*	109*

* Visibly coagulated

These experiments show that the opalescence at 20° increases slowly to an almost constant value in an hour. Heating to 60° not only hastens the attainment, but results in a still greater opalescence, which, however, falls off on continued heating. There is, moreover, marked evidence of coagulation after 30 minutes.

Similar measurements made at 40° indicated that the rapid coagulation observed at 60° did not then occur. A series of experiments covering a considerable range of concentration

ties of sodium chloride solutions. They were heated for various times at 40° and then cooled and read. For comparison, observations were made on similar solutions kept for 60 minutes at 20° and not heated, and these together with the others are included in Table VI.

TABLE VI.—CHANGE OF OPALESCENCE WITH TIME AT 40°.

Conc X 10 ³ M	Total weight Cl mg	Time, min Temp	60	30	60
			20° %	40° %	40° %
0.37	0.0053		69	(100)	99
2.00	0.0284		71	(100)	98
9.0	0.128		87	(100)	98
9.0	0.128		88		99
9.0	0.128	87	91		104
9.0	0.128		84		96
30.0	0.426		95	(100)	100
30.0	0.426		91	91	99
30.0	0.426		94		100

* Visibly coagulated

These results confirm our previous conclusion that at room temperature the maximum opalescence is not by any means attained within an hour, particularly at the lower concentrations. They further show that over a wide range of concentrations a substantially constant opalescence is attained after 30 minutes' heating at 40°, and that further heating at this temperature is without noticeable effect.

It is important, however, to know how long this maximum opalescence developed by heating will persist unchanged at room temperature. To determine this a similar series of suspensions of different concentrations was prepared, heated as usual at 40° for 30 minutes, cooled and allowed to stand. At intervals samples were pipetted out and compared with freshly prepared suspensions. The results are given in Table VII.

TABLE VII.—EFFECT OF STANDING AT ROOM TEMPERATURE AFTER HEATING.
Samples Heated 30 Min. at 40°.

Conc X 10 ³ M	Total weight Cl Mg	Min	Percentage Opalescence				
			Time of standing after heating				
			0	10	90	180	300
2.00	0.0284	99				97	101
2.00	0.0284	100		102	102	96	
9.0	0.128	99			100	85	74
9.0	0.128	100				89	
30.0	0.426	101	99	84	71		50

These results show that faintly opalescent suspensions are stable for several hours, but that the strongly opalescent suspensions produced by high concentrations show a perceptible decrease after an hour. These latter should then be read within a half hour after cooling.

tion in a water bath kept at 40° for at least 30 minutes. It was then cooled rapidly to room temperature and within 30 minutes compared in a nephelometer with suitable standards similarly prepared.

This technique appears superior to that of Wells in two respects—it not only develops a maximum and more constant opalescence, particularly in the case of the more concentrated solutions, but it also is simpler in that the same procedure is applicable over a wide range of concentrations. The results in Tables VI and VII, where the suspensions were treated by this standard technique, show that a maximum deviation of 4% for any single analysis, and a still greater accuracy for the average of several analyses can be counted upon. This estimate is confirmed by the results in Table VIII, and by a large number of other analyses not cited here.

The Effect of Light on Opalescence.

Exposure to direct sunlight produces so great a change in the color and the nature of the silver chloride suspensions that nephelometric readings on such samples are quite out of the question. Wells states that he could detect no effect of a 2-hour exposure to the light of the nephelometer on the opalescence of his suspensions. We find that with suspensions prepared and "developed" as above, exposure to diffuse daylight has a perceptible effect, especially in the more concentrated solutions. This is shown by experiments collected in Table VIII.

TABLE VIII—EFFECT OF DIFFUSE DAYLIGHT ON OPALESCENCE
Temperature, 20°

Molar conc X 10 ³	Total wt. Cl Mg		Time min	"	"	120	180
2.00	0.0284	%	}	in dark	(100)	102	96
		Opalescence		in light	102	99	94
9.0	0.128	%	}	in dark	(100)	99	97
		Opalescence		in light	102	98	91
30.0	0.426	%	}	in dark	(100)	100	92
		Opalescence		in light	96	92	82

It is evident that the opalescence decreases more rapidly with the time when the suspensions are exposed to light than when they are kept in the dark, particularly in the more concentrated solutions.

Opalescence in Other Solvents

The solvent so far employed was always an approximate 50% ethyl alcohol-water mixture. It appeared of interest to compare the opalescence developed by the same amount of silver chloride in other solvents. Suspensions were, therefore, prepared as before, except that in place of the alcohol, in one case water and in another glacial acetic acid was substituted. This gave, on the one hand, a suspension in water and, on the other hand, in approximately 50% acetic acid solution. The suspensions were all heated for 35 minutes to 40°, cooled rapidly and compared with

a suspension in a 50% alcoholic solution, treated in a similar way. The results expressed in percentages of the opalescence of the 50% alcoholic solution are given in Table IX.

TABLE IX—OPALESCENCE IN VARIOUS SOLVENTS.

Solvent	Molar conc $\times 10^4$	62	23
50% alcohol.		(100)	(100)
Water.		115	115
50% acetic acid		101	102

The opalescence in 50% acetic acid is substantially the same as in 50% alcohol; that in water is somewhat greater, but no effect of concentration is evident.

Summary.

It has been shown that

(1) In a 50% alcohol-water solution, heating silver chloride suspensions of widely differing concentrations to 40° for 30 minutes after precipitation, produces a more intense and constant opalescence than can be attained at room temperature, further heating for 30 minutes at 40°, or standing at room temperature for an hour produces no perceptible change in this opalescence

(2) Using this technique, chlorides in such solutions can be estimated with an average deviation of about 3 to 4% over concentrations ranging between 4 and $300 \times 10^{-4} M$

(3) Opalescence in such solutions decays more rapidly in diffuse daylight than in the dark

(4) The opalescence of the same quantity of silver chloride in water is about 15% greater than in 50% alcohol or 50% acetic acid.

Certain phases of this problem are being studied further by Meldrum.

WASHINGTON, D C

[CONTRIBUTION FROM THE INSECTICIDE AND FUNGICIDE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE]

THE ARSENATES OF CALCIUM. I. EQUILIBRIUM IN THE SYSTEM ARSENIC PENTOXIDE, CALCIUM OXIDE, WATER AT 35° (ACID SECTION).

By C. M. SMITH

Received December 9, 1919

Owing to the commercial importance which calcium arsenate has recently assumed as an agricultural spray material more detailed knowledge of its chemical and physical properties has become essential. One of the most important questions in relation to a spray for use on vegetation is its behavior with water, which may and often does result in the liberation of so called "soluble" arsenic—including in that term not only the arsenic which may be present as a soluble impurity but also that which

comes from any decomposition or solution of the spray material by the water with which it is in contact.

It appeared that the best way to treat this question was by a study of the general equilibrium conditions in the system, and the application of the phase rule criteria to the interpretation of the results.

This system is one of 3 components, calcium oxide, arsenic oxide, and water. According to the phase rule, a 3-component system will always behave in such a way that the sum of the number of phases and the degrees of freedom will be 5. For the purpose of the investigation, only those conditions under which at least 3 phases—gas, solution, and solid—exist are of interest to us. By working at constant temperature the system may be reduced to one degree of freedom, in which state the existence of one solid phase will be indicated by variation of the solution, while the appearance of a second solid phase will render the system invariant and result in the production of a constant solution. Consequently, if various empirical mixtures are made up and allowed to come to equilibrium, analysis of the solutions and solid phases will serve to establish the limits within which the different compounds can exist.

Owing to the fact that arsenic acid is extremely soluble, while calcium oxide is only sparingly so, the entire range of experiments could not be covered in the same way. Consequently the subject was divided into two sections, which have been designated the acid and basic sections, and the two series of solutions arranged so they overlap. The acid region forms the subject of this paper, the basic region being covered in a paper to appear subsequently.

In order to obtain pure calcium oxide, that used was all prepared from calcium chloride by two precipitations with ammonium carbonate and subsequent ignition in an electric muffle. By this means a product was obtained containing only 0.04% of magnesium oxide and 0.08% of carbon dioxide, and no more than mere traces of any other impurities.

The arsenic acid was purified as follows. Ordinary commercial acid containing about 75% of ortho arsenic acid was concentrated by boiling until the boiling point rose to 150°. It was then cooled and "seeded" with a crystal or two of solid arsenic acid ($\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$). This caused the separation, in a short time, of the main bulk of arsenic acid as the above mentioned hydrate. (The "seeding" is absolutely necessary, for supersaturated solutions have been kept in the laboratory for 2 years without spontaneous separation having occurred. The first crop of crystals was obtained by cooling some supersaturated solution to about -10°.) If the solution is left undisturbed after "seeding," the crystals form large enough to be filtered on a Büchner funnel without the use of any filter medium. (Paper could not be used on account of the destructive action of the strong arsenic acid upon it.) Six such recrystallizations were

carried out by the method of combining filtrates and residues which gave a product practically free from all common impurities. (It may be mentioned that the chief impurity in the commercial acid was an extremely finely divided suspension of oxide of iron, which readily passed through the Buchner funnel.) This crystallized product melts at about 36° . It is hygroscopic and is not suited for weighing definite amounts, but it is very readily soluble in water, and solutions of any desired strength up to about 74% of arsenic oxide may be prepared from it.

The experiments which form the immediate subject of this paper were planned as follows: The arsenic acid was prepared in the form of a thick sirupy solution, $d\ 2.31$ and containing 74.8% of arsenic oxide. To a series of 2-ounce bottles, numbered from 1 to 15 inclusive, were added successively increasing amounts of the strong acid, the amounts being so arranged that on dilution of each with water to a volume of 40 cc. there was obtained a series of arsenic acid solutions ranging from 5% to 75% of arsenic oxide in steps of 5%. Both strong acid and water were measured from a buret, and rather crudely, for an exact knowledge of the composition was not necessary. To these solutions was now added powdered calcium oxide in small quantities until the acid was saturated, and then about one g. additional. This insured the presence of 2 or 3 g. of solid residue. The bottles were then securely stoppered and attached to a rotating machine which was immersed in a water bath maintained at 35° . The machine was run continuously day and night, and tests of one solution at the end of 10 days and 17 days showed that it had reached equilibrium. Since the machine contained at the same time the basic experiments, which were much slower in reaching equilibrium, the whole lot was not removed for about 3 months. In that time the maximum variation of temperature was about 2° , with an average daily variation of less than 0.5° .

When the samples were removed from the shaking machine they were filtered as quickly as possible, using a Gooch crucible containing a disc of hardened filter paper. When the liquid had drained out, it was recovered while the wet residue was transferred to a weighing bottle, weighed, and dissolved in a known amount of dil. hydrochloric acid. The amount of the latter used was figured to give a solution of a strength suitable for analysis. The densities of all the filtrates were determined at 35° , correction being made for buoyancy of air. All analyses were made on weighed samples, but the density data of the filtrates permitted recalculation to volume figures, which has been done.

The methods of analysis used were as follows. For calcium oxide a suitable aliquot was taken, the acidity reduced if necessary with ammonia, the solution heated to boiling, and 50 cc. of boiling ammonium oxalate solution (40 g. per liter) run in very slowly from a pipet. This

procedure quantitatively separates the lime from the arsenic, and produces a precipitate so granular that it settles almost immediately and may be filtered after half an hour or so. After filtration and washing, the precipitate was titrated with standard permanganate solution. For arsenic, a suitable weight of sample was evaporated to about 10 cc. on the steam bath, cooled, 25 cc. of conc. hydrochloric acid added, then 10 cc. of water containing one g. of potassium iodide, then 25 cc. of ammonium chloride solution (200 g. per liter), and the liberated iodine finally titrated with standard thiosulfate solution. The results of these analyses are given in Table I

TABLE I

Expt.	Composition of wet residue % by wt		Composition of solution % by wt		Density of solution	Composition of solution G. per liter		Molecular ratio in solution $\frac{\text{CaO}}{\text{As}_2\text{O}_3}$
	CaO	As ₂ O ₃	CaO	As ₂ O ₃		CaO	As ₂ O ₃	
1	18.24	31.10	0.096	0.198	0.996	0.956	1.372	1.99
2	22.49	45.93	0.702	2.711	1.025	7.20	27.79	1.06
3	22.16	46.14	1.903	7.98	1.04	20.74	87.0	0.98
4	21.12	44.89	3.206	12.97	1.157	37.09	150.1	1.01
5	21.66	46.42	4.59	18.70	1.242	57.0	232.3	1.01
6	20.96	45.31	4.64	19.99	1.261	58.5	252.1	0.95
7	22.31	48.09	5.34	21.97	1.300	69.4	285.6	1.00
8	15.56	62.91	6.54	28.78	1.413	92.5	405.4	0.94
9	14.44	62.02	5.34	35.03	1.48	79.0	518.4	0.62
10	12.42	60.77	4.07	43.43	1.590	64.7	690.5	0.38
11	11.66	63.00	2.95	50.30	1.697	50.1	853.6	0.24
12	6.56	59.98	1.87	55.43	1.795	33.6	995.0	0.14
13	7.64	66.39	0.822	62.66	1.975	16.2	1237.0	0.05
14	7.36	70.92	0.135	71.04	2.167	2.93	1539.0	0.008
15	4.21	77.92	0.114	72.14	2.417	2.53	1599.0	0.006

Since it was impossible to remove all adhering mother liquor from the solid precipitates, the following well known graphical scheme was used for finding the composition of these solids. If the points representing any solution and its corresponding wet residue are connected by a line, this line produced passes also through the point representing the dry residue. Two such lines will converge at this latter point, provided the solid material remains the same. However, to establish definitely that it is a fixed compound it is necessary that a third line converge at this point. This method has been followed in Fig. 1. In the presentation of the results rectangular coordinates are used instead of the possibly more common triangular ones because of greater ease of interpretation. The percentage of calcium oxide has been plotted against the percentage of arsenic oxide, the ordinate scale being given a relative magnification of 2.5 in order to bring out the relationship more clearly.

Now consider the results of Expts. 2 to 7 inclusive. It is seen that the solution results fall upon a straight line, AB, while the lines drawn through

solutions and residues actually converge to a more or less definite point. Owing to the fact that the lines are not very convergent, it is difficult to pick the point of convergence from the graph. However, by applying the method of least squares, the most probable position of this point was found to correspond to 27.1% of calcium oxide and 55.3% of arsenic oxide.¹

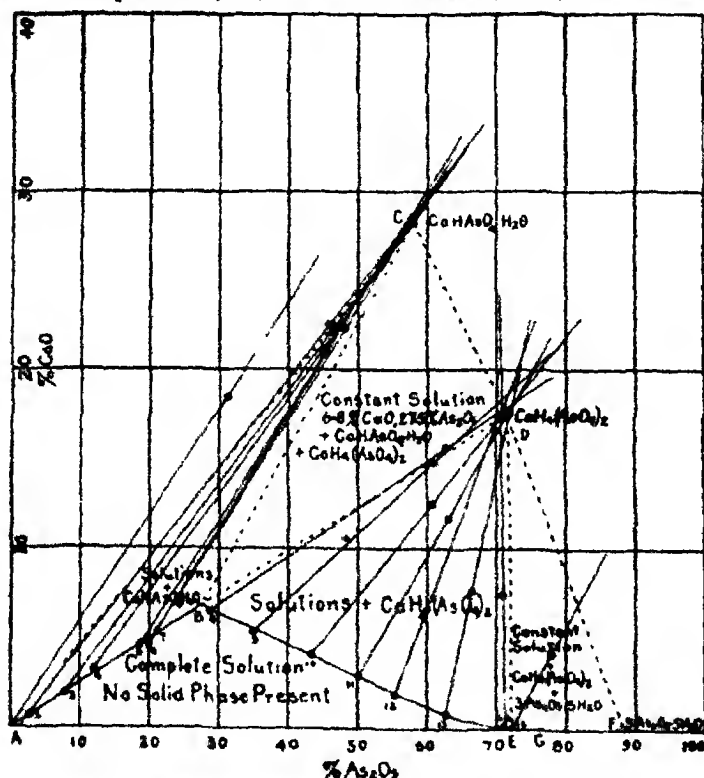


Fig. 1.—Equilibrium in the system As_2O_5 - CaO - H_2O at 35°

These figures are almost exactly those corresponding to the formula, $\text{CaHAsO}_4 \cdot 1.5\text{H}_2\text{O}$. Such a formula has been ascribed to products obtained by Turner,² Kotschubey,³ and Debray,⁴ but De Schulten's experiments,⁵

¹ This calculation was based on the following assumptions that all the individual analyses were of equal weight; that the lines should be given weight proportional to the length between their determining points, and finally that the most probable point of convergence should be taken as the point where the sum of the squares of the weighted perpendicular distances from the various lines is a minimum

² *Edinburgh J. Sci.*, 3, 306 (1825).

³ *J. prakt. Chem.*, 49, 182 (1850).

⁴ *Ann. chim. phys.*, [3] 61, 427 (1861).

⁵ *Bull. soc. franc. min.*, 36, 22 (1903).

as well as our own¹ have not confirmed it. The two well defined natural hydrates have the formulas $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ and $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ (baldingerite and pharmacolite). The probable error in the point of convergence is great enough to include both of these compounds, but examination by the petrographic microscope shows that the former is the compound actually present. Consequently the compound of the formula $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ can be in equilibrium only with solutions along the line AB.

Passing now to Expts. 8 to 14 inclusive, it is found that the solutions range along another approximately straight line BE, while the solution-residue lines converge to a point the most probable location of which has been calculated to be that corresponding to 17.7% of calcium oxide and 71.4% of arsenic oxide. These are quite close to the theoretical values, 17.4 and 71.4, for the compound of the formula $\text{CaH}_4(\text{AsO}_4)_2$, monocalcium orthoarsenate.² Because of the wider divergence of these lines, the calculated values have much greater weight than in the former case, and furthermore since we have been able to produce a compound of this formula by other means, its existence here is definitely established.

The point B at which the two solution curves AB and BE intersect, represents the constant solution which exists in the presence of both solid phases. It is unfortunate that none of the experiments happened to fall at this point, but the graph shows it to be located at a position approximately corresponding to 6.8% of calcium oxide and 27.5% of arsenic oxide. Had any experiment fallen here its representative line would have traversed the region BCD and cut the dotted line CD at a point representing the composition of the mixture of solids present.

Expt. 15 was made by putting some calcium oxide into a mushy mixture of crystalline arsenic acid ($\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$) and its saturated solution, in an attempt to determine the constant solution in contact with both calcium arsenate and arsenic acid. The line representing this experiment does not converge to the point D, showing that a new phase has appeared, and furthermore the position of the wet residue point shows that the second phase is not the arsenic acid started with ($\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$). Menzies and Potter³ state that they were able to prepare only two hydrates of arsenic pentoxide, the 1,4-hydrate just mentioned and a 3,5-hydrate ($3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$). They also state that the latter compound is the more stable above 29.5°. This explains the transposition of the arsenic acid originally taken into the other hydrate. The point E, therefore, represents the constant solution in contact with monocalcium orthoarsenate

¹ A subsequent paper will describe the various compounds of CaO , As_2O_5 and H_2O , the methods of their preparation in crystalline form and a study of their properties.

² This compound has not previously been reported, although Hoermann (Inaugural Dissertation, "Beitrag zur Kenntniss der Pyro- und Meta-Arsensäure" Erlangen, 1879) has described its monohydrate.

³ THIS JOURNAL, 34, 1469 (1912).

and the 3.5-hydrate. It contains 0.114% of calcium oxide and 72.14% of arsenic oxide, the latter figure being in close agreement with the figure 73.0 given by Menzies and Potter for the solubility of the 3.5-hydrate at 35°.

It may be seen from the graph that the points representing solid phases and constant solutions have been connected by dotted lines. These lines divide the entire chart into various regions, which permit of predicting the behavior of any empirical mixture of calcium oxide, arsenic oxide, and water when kept at 35°. For instance any empirical mixture whose representative point falls within the area BDE will separate into the solid monocalcium orthoarsenate and a solution represented by some point on the line BE. Likewise, any empirical mixture whose representative point falls within the region ABE will form a solution with no residue.

There remains to be considered one line, that representing Expt. 1. This does not pass near the point C, showing that there must be present some compound more basic than dicalcium orthoarsenate monohydrate. The equilibrium conditions in this system covering the basic region will be presented in a subsequent paper.

It appears worthy of note that the line AB, representing solutions in equilibrium with dicalcium orthoarsenate monohydrate, if extended, passes very close to the point D representing monocalcium orthoarsenate. In other words, dicalcium orthoarsenate monohydrate is stable only (apparently) in solutions of monocalcium orthoarsenate. This is brought out plainly in the last column of Table I, where it is seen that the average value of the molecular ratio of the solutions from Expts. 2 to 7 inclusive is 0.99.

Summary.

1. The general equilibrium relations in the 3-component system arsenic pentoxide, calcium oxide, and water have been investigated for the acid region at 35° and the phase rule criteria applied to the interpretation of the results.

2. Two compounds have been found to be stable under the conditions of the experiment, dicalcium orthoarsenate monohydrate, $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$, identical with the natural mineral haidingerite, and monocalcium orthoarsenate $\text{CaH}_2(\text{AsO}_4)_2$, existing below and above, respectively, an acid concentration corresponding to 27.5% arsenic pentoxide.

W. G. ZIMMERMAN, D. C.

NOTE.

Correction.—The diagram on page 70 of the January, 1920, Journal was inverted. The correct orientation is shown herewith.

H. W. FOOTE.

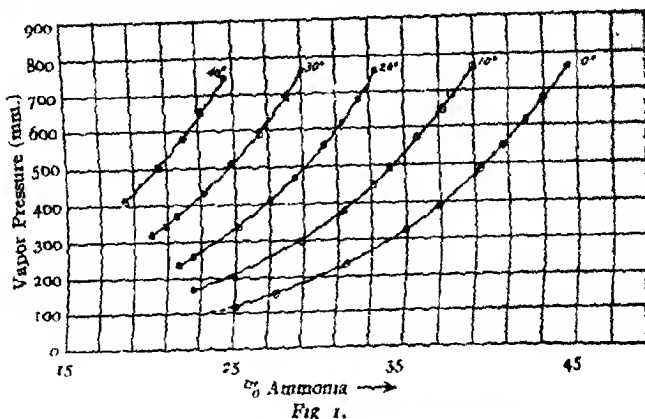


Fig. 1.

[CONTRIBUTION FROM THE GAS MASK RESEARCH SECTION, CHEMICAL WARFARE SERVICE, U S A]

QUANTITATIVE DETERMINATION OF TRACES OF DICHLORO-ETHYLSULFIDE (MUSTARD GAS) IN AIR.¹

BY MAX YABLICK, G ST. J. PERROTT AND N. H. FURMAN

Received March 19, 1919

A Nephelometric Method Using Selenious Acid.

This paper deals with a very sensitive method for analyzing air mixtures containing traces of dichloro-ethylsulfide. The method was developed as the result of a need for a qualitative test for mustard gas which should indicate the presence of dangerous amounts of the substance in the air. When it is known that concentrations of the vapor as low as 0.0005 mg. per liter (0.08 p. p. m.) will cause discomfort on exposure for 25 minutes and concentrations between 0.001 mg. per liter and 0.005 mg. per liter (0.2 p. p. m. and 0.8 p. p. m.) will cause skin burns if exposure is as long as 30 minutes, it can be seen that an extremely delicate indicator is necessary to vie in sensitivity with the physiological test.

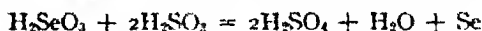
Briefly, the method consists in reducing a 1% solution of selenious acid in 1:1 sulfuric acid by means of the dichloro-ethylsulfide vapor to an orange-red suspension of selenium, the solution being heated to about 85° to facilitate the reaction. In this way amounts of the substance as low as 0.005 mg. can be detected.

¹ Approved for publication by the Director of the Chemical Warfare Service.

The amount of the suspension produced is nearly directly proportional to the amount of dichloro-ethylsulfide present. Amounts of the compound from 0.10 mg. to 0.01 mg. can be estimated with a fair degree of accuracy by nephelometry.

The method has had a variety of uses, among which may be mentioned the detection of the presence of mustard gas in field and factory, securing of quantitative data as to the persistency of the gas over contaminated soil, and determining the permeability of protective fabrics to the vapor and liquid.

Schulze¹ first prepared a hydrosol of selenium in 1885 by reduction of a solution of selenious acid with sulfurous acid ($\text{H}_2\text{SeO}_3 : 2\text{SO}_2$)



With changed proportions, reduction is incomplete. When an excess of sulfur dioxide is present $\text{H}_2\text{SeS}_2\text{O}_6$ is formed, with excess of selenium dioxide $\text{H}_2\text{Se}_2\text{SO}_6$ is formed. The reaction takes place more completely in the presence of hydrochloric acid. Hydroxylamine and hydrazine salts also reduce selenious acid with precipitation of metallic selenium.² Glucose, formic acid, formaldehyde and a number of organic acids and aldehydes have been found to have a similar action.³

We have not investigated the mechanism of the reduction of our selenious acid reagent by dichloro-ethylsulfide. A possible explanation is that the nascent sulfur dioxide set free by the reaction between warm sulfuric acid and dichloro-ethylsulfide effects the reduction. The decomposition products of the dichloro-ethylsulfide may possibly play some part in the reaction.

Apparatus and Solutions Used.

In our work the nephelometric comparison method described by Kober has been employed.⁴ A nephelometer colorimeter made by the Klett Manufacturing Co., New York City, was used.

In order to estimate the strength of suspensions produced by unknown amounts of vapor it was necessary to devise some means of preparing reproducible standard suspensions equivalent to known amounts of the vapor. For this purpose standard solutions of dichloro-ethylsulfide were prepared as follows: I. A stock solution made by dissolving about 0.01 g. dichloro-ethylsulfide in 100 cc. of cold 1:1 (by volume) sulfuric acid; II. For use, 10 cc. of Solution I was diluted to 100 cc. with cold 1:1 sulfuric acid. This solution was found to remain unchanged for several weeks.

¹ H. Schulze, *J. prakt. Chem.*, [2] 32, 390-407 (1885).

² Jannasch and Müller, *Ber.*, 31, 2388 (1898).

³ Oechaner, de Coninck and Chauvenet, *Compt. rend.*, 141, 1234 (1905).

⁴ *J. Ind. Eng. Chem.*, 10, 556-63 (1918)

The selenious acid reagent contained 1.0 g. of selenium dioxide per 100 cc. of cold 1:1 sulfuric acid.

The solutions of dichloro-ethylsulfide were used to prepare standard suspensions of selenium corresponding to a suitable range of weights of dichloro-ethylsulfide per 20 cc. of the suspension medium which was 1:1 sulfuric acid.

Procedure in Use of Nephelometer and Method for Obtaining a Standard Curve.

In preparing the nephelometric curve shown in Fig. 1, suitable amounts of Solution II were pipetted out so that the selenium suspensions corresponded to 2, 1.5, 0.9, 0.8, etc., times the value of the standard. The standard suspension corresponded to 0.045 mg. of dichloro-ethylsulfide per 20 cc.

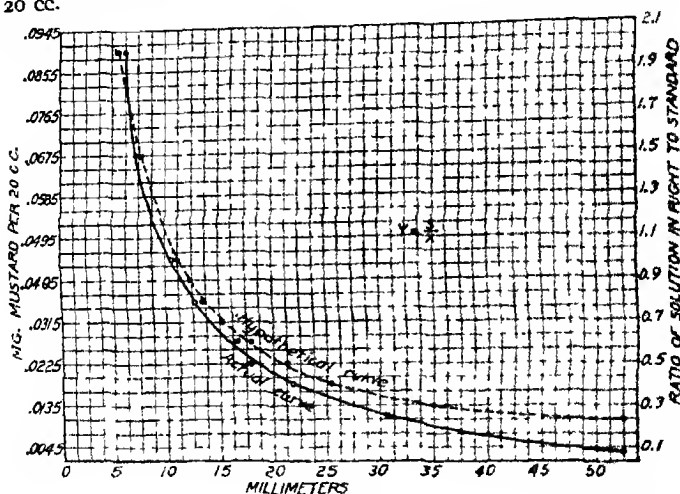


Fig. 1.

The method of preparing the standard and other suspensions may be illustrated from the following data.

Dichloro-ethylsulfide Solution I contained 0.0078 g. per 100 cc. Dichloro-ethylsulfide Solution II contained 0.00078 g. per 100 cc. Therefore, 5.8 cc. of Solution II contained 0.045 mg. of dichloro-ethylsulfide. To 5.8 cc. of dichloro-ethylsulfide Solution II were added 4.2 cc. of 1:1 sulfuric acid and 10 cc. of selenious acid reagent. The resulting mixture was agitated until uniform. It was then maintained at $85^{\circ} \pm 5^{\circ}$ for 10 minutes, and cooled to room temperature.

The resulting selenium suspension was then placed in both cups of the nephelometer, the left-hand platform being set at 10 mm. The reading of the right-hand platform was taken after adjusting the height

of the column of liquid until equal intensity of illumination was obtained in both fields of the eyepiece.

In the right-hand cups were then placed suspensions containing 2.0, 1.9, 1.5, etc., 0.9, 0.8, etc., times as much dichloro-ethylsulfide per 20 cc. as the standard contained, the respective readings being noted.

In each case the cup was rinsed with 3 portions of the solution to be tested, and the outside of the cup washed with distilled water and dried before the readings were taken.

In Fig. 1 is a curve obtained by plotting the mean of readings taken on different days, and upon standards made from several different dichloro-ethylsulfide solutions. The hypothetical curve is based on the assumption that the scale reading varies inversely as the amount of suspended material present.

The close proximity of the two curves indicates that the reaction between selenious acid and dichloro-ethylsulfide is very nearly complete under the conditions outlined.

A few results will serve to show the consistency of the readings.

Date	Dichloro-ethylsulfide solution	Ratio of standard solution to solution in right.		
		1 1	1 0.5	1 0.2
July 25	A	11 1	17 8	30.5
July 26	A	10 7	.	.
July 29	B	10 3	.	.
		11 3	17.5	33.0
July 30	B	10 9	17.2	32 0
Aug 8	C	10 0	17 0	33 0
Aug. 12.	D	10 7	16 0	30 0
Aug 14	D	10 5	17 0	

Solutions were prepared by one observer, in a manner similar to that in which the solutions mentioned above were made, and the readings were taken by another observer.

	Dichloro-ethylsul- fide taken Mg.	Dichloro-ethylsul- fide found, Mg.	Error. Mg.
1	0.0450	0.0428	-0.0022
2	0.0312	0.0347	+0.0035
3	0.0234	0.0243	+0.0009
4	0.0150	0.0170	+0.0020
5	0.0078	0.0079	+0.0001

After the foregoing method for determining the strength of solutions of dichloro-ethylsulfide had been worked out, our attention was turned to the question of estimating amounts of the vapor present in air-dichloro-ethylsulfide mixtures and to find insofar as our limited time allowed the optimum conditions for absorption which should best combine sensitivity and reproducibility.

Factors Affecting Accuracy of Method.

Several series of experiments were run, first to determine the reproducibility of the standard method using a 1% solution of selenium dioxide in 1:1 sulfuric acid; second, to determine the effect of varying the amount of sulfuric acid in the cold absorbing solution; third, to find the effect of varying the strength of an aqueous solution of selenium dioxide; fourth, to determine the stability of the selenious acid solution and of the dichloro-ethylsulfide solution used in preparing standard suspensions. Unavoidable circumstances have prevented our making the investigation complete. We are able to say, however, that we have developed a quantitative method for determining amounts of dichloro-ethylsulfide in air from 0.1 mg. to 0.01 mg. with a maximum error of about 0.005 mg.

Apparatus Used in Producing Low Concentration of Dichloro-ethylsulfide Vapor.

The apparatus shown in the figure was arranged to deliver one liter per minute of an air mixture containing about one part per million of dichloro-ethylsulfide

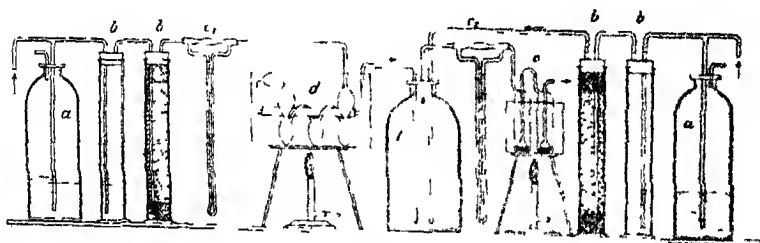


Fig. 2

a.—constant pressure bottle
b.—air-purifying bottle
c.—flow meter

d.—mustard bubbler in bath at 20°.
e.—selenious acid bubbler in bath at 85°.
f.—mixing jar

The bulb D contains dichloro-ethylsulfide redistilled *in vacuo* and is kept in a water bath at 20°. Air purified by passing through sulfuric acid and a charcoal, soda-lime mixture is passed through the liquid in bulb D at a rate of 11 cc. per minute as measured by the flowmeter C.¹ The saturated air passes into the mixing chamber F where it is mixed with pure air sufficient to bring the entire flow up to 1000 cc. per minute as measured by the flowmeter C₂. The air mixture, containing 0.0062 ± 0.0004 mg. per liter,² now passes through the absorbing solution in the bubblers E.

¹ Rates and concentrations varying slightly from this figure were used in several determinations described later

² Calculated from British data on vapor pressure of dichloro-ethylsulfide.

Treatment of Absorbing Solutions.

Ten cc. of the absorbing agent used is placed in the bubbler and the mixture passed through it for 10 minutes. Ten cc. of a solution of selenious acid in sulfuric acid is then added, the sulfuric acid being of such strength as to make the resulting mixture 1:1 sulfuric acid and the selenious acid present in the same per cent. as in the original 10 cc. of absorbing agent; for example, if 10 cc. of a 1% solution of selenium dioxide in water were used as the absorbing medium, then 10 cc. of a 1% solution of selenium dioxide in conc. sulfuric acid is added making 20 cc. of a 1% solution of selenium dioxide in 1:1 sulfuric acid.

The solution is then heated for 10 minutes in a bath at 85°, cooled, and the strength estimated by comparison with a standard solution prepared as previously described. Data are given in terms of milligrams per liter, *i. e.*, 1/10 of the actual amount of dichloro-ethylsulfide measured.

1. Using a solution of 1% selenium dioxide in 1:1 sulfuric acid, to find the effect of passing the vapor through the hot and cold solution.

Hot solution mg./liter	Deviation from mean	Hot solution, mg./liter	Deviation from mean
0.0063	+0.0001	0.0056	-0.0003
0.0062	-0.0000	0.0061	-0.0002
0.0067	+0.0005	0.0053	-0.0006
0.0058	-0.0004	0.0063	+0.0004
0.0060	-0.0002	0.0058	-0.0001
0.0063	+0.0001	0.0060	+0.0001
0.0065	+0.0003	0.0062	+0.0003
Av., 0.0062	0.0002	0.0059	0.0003

Solutions heated 10 min at 85° before taking nephelometric readings.

Amount actually present as calculated from vapor-pressure measurement = 0.0062 ± 0.0004

From the above data it is evident that there is no apparent difference between results when hot and cold selenious sulfuric acid solutions are used as absorbents.

2. To find the effect of varying the amount of sulfuric acid in cold selenious sulfuric acid solution.

Results show less deviation from the mean and more closely approach the theoretical, when sulfuric acid is present in the original absorbing solution.

3. To find the effect of increasing the strength of a water solution of selenium dioxide.

It had been noticed in a qualitative way that very concentrated water solutions of selenium dioxide gave a heavier precipitate for an equal amount of dichloro-ethylsulfide than did dilute solutions. To find the magnitude of this change in sensitivity, a concentration of 0.0062 mg. per liter of dichloro-ethylsulfide was passed through water solutions

1% SeO ₂ in conc. H ₂ SO ₄ , mg./liter	Deviation from mean	1% SeO ₂ in 1:1 H ₂ SO ₄ , mg./liter	Deviation from mean	1% SeO ₂ in H ₂ O, mg./liter	Deviation from mean.
0.0058	+0.0004	0.0053	-0.0005	0.0063	-0.0010
0.0051	-0.0003	0.0060	+0.0002	0.0081	+0.0008
0.0053	-0.0001	0.0068	+0.0010	0.0077	+0.0004
0.0061	+0.0007	0.0057	-0.0001	0.0069	-0.0004
0.0060	+0.0006	0.0059	+0.0001	0.0091	+0.0018
0.0059	+0.0005	0.0055	-0.0003	0.0068	-0.0005
0.0047	-0.0007	0.0062	+0.0004	0.0074	+0.0001
0.0048	-0.0006	0.0061	+0.0003	0.0082	+0.0009
0.0053	-0.0001	0.0060	+0.0002	0.0065	-0.0008
0.0050	-0.0004	0.0054	-0.0001	0.0063	-0.0010
Av. 0.0054	0.0004	0.0058	0.0004	0.0073	0.0008

Amount actually present calculated from vapor-pressure measurements = 0.0062 ± 0.0004

NOTE.—The solutions after absorbing the vapor were made to contain 1:1 H₂SO₄, heated for 10 minutes at 85° and cooled before being read with the nephelometer.

of different strengths of selenious acid for 10 minutes and the resulting solution developed as before and estimated in comparison with a standard suspension made from a 1% selenious acid solution. In this way we obtained figures indicating the relative amounts of suspension produced in various strength solutions by a constant quantity of dichloro-ethylsulfide. Experiments were run both with the solution hot and cold during absorption. Each result is the average of 5 determinations.

0.0062 mg./liter present

% SeO ₂	Amount found			
	Solution, hot, mg./liter	Error	Solution cold, mg./liter	Error
10.00	0.0380	+0.0318	0.0072	+0.0010
5.00	0.0213	+0.0151	0.0078	+0.0016
4.00	0.0184	+0.0122	0.0079	+0.0017
3.00	0.0130	+0.0068	0.0074	+0.0012
2.00	0.0093	+0.0031	0.0069	+0.0007
1.00	0.0067	+0.0005	0.0064	+0.0002
0.50	0.0033	-0.0029	0.0053	-0.0009
0.25	0.0014	-0.0048	0.0049	-0.0013
0.125	0.0012	-0.0050	0.0027	-0.0035

Results show that a very large increase in sensitivity is obtained by using a concentrated hot solution of selenium dioxide in water. The 10% solution gives about 10 times as dense a suspension as is obtained by the method first described where a 1% solution of selenium dioxide in 1:1 sulfuric acid is employed. Results at these high percentages, however, are very erratic and cannot be duplicated to within 50%, and in general results using aqueous solutions as absorbents are not duplicable with any degree of accuracy. Using a cold aqueous solution, the differ-

ence is very much less marked, the 10% solution giving only about 1.3 greater density of suspension than the standard.

4. Aging of the selenious acid solution.

1% SeO_2 in 1:1 H_2SO_4 in each case 0.055 mg. of dichloro-ethylsulfide was actually present.

Date of test.	Solution made Oct. 24 Mg.	Solution made Oct. 16. Mg.
Oct. 24.....	0.038	0.053
Oct. 25.....	0.057	0.059
Oct. 28.....	0.058	0.057
Oct. 29.....	0.055	0.053
Oct. 30.....	0.055	0.052

This series of results was obtained by passing air-dichloro-ethylsulfide mixture from the standard machine through 20 cc. of selenium acid solution contained in the bubbler and kept in a bath at 85°. Each figure is the average of 5 determinations.

Data show that the selenious acid solution should not be used until 24 hours after it is made up, but that after this time the solution is stable for at least two weeks.

5. Aging of standard solution of dichloro-ethylsulfide.

A standard solution of dichloro-ethylsulfide was made up as previously described. This was tested at intervals of one week by comparison with a suspension of selenium made by passing 0.045 mg. of dichloro-ethylsulfide vapor into 20 cc. of selenious acid reagent as previously set forth. This was then compared with a suspension made by adding an amount of the standard solution containing 0.045 g. of dichloro-ethylsulfide to 10 cc. of the selenious acid reagent and making the whole up to 20 cc. with 1:1 sulfuric acid. The same procedure was carried out with a standard solution made up the same day. Each figure is an average of 5 determinations.

Age of standard, Weeks.	Amount found Mg.	Amount found, using freshly made standard. Mg.
1.....	0.046	0.046
2.....	0.045	0.045
3.....	0.043	0.046
4.....	0.046	0.044

Variations are within the experimental error of the method. Apparently little deterioration of the standard solution takes place over a period of 4 weeks.

Discussion.

The temperature at which the solution is heated in process of "developing" can vary 5° in either direction without affecting the character of the suspension. The method is remarkably free from the necessity for extreme purity of original solutions, cleanliness of glassware, etc., which obtains in silver halide nephelometry.

Attempts to determine the strength of the suspension colorimetrically were not successful.

It was not found possible to use good solvents for dichloro-ethylsulfide as absorbing solutions and then determine the strength by our method, for the reason that the only suitable solvents (alcohol and acetic acid) reduced the selenious acid to some extent.

The selenious acid reagent is not specific to mustard gas. Arsine and the substituted arsines and several other toxic gases react with it vigorously.

Selenious acid may have a possible use as an indicator in oxidation-reduction reactions.

We wish to express our appreciation of the work of A. E. Plumb, who made a great many of the determinations.

Summary.

A solution of selenious acid in 1:1 sulfuric acid is reduced by traces of dichloro-ethylsulfide giving an orange red suspension of selenium. About 0.005 mg. of dichloro-ethylsulfide can be detected in this manner. A nephelometric procedure for determining amounts of the substance between 0.1 mg. and 0.01 mg. with a maximum error of 0.005 mg. has been developed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE OCTET THEORY OF VALENCE AND ITS APPLICATIONS WITH SPECIAL REFERENCE TO ORGANIC NITROGEN COMPOUNDS.

BY IRVING LANGMUIR

Received July 7 1919

The octet theory of valence¹ leads to structural formulas for organic compounds which are identical with those given by the ordinary valence theory whenever we can assume a valence of 4 for carbon, 3 for nitrogen, 2 for oxygen and one for hydrogen and chlorine. This follows from the following reasoning:

Let us represent by E the number of electrons in the shell of an atom. For the elements of the two short periods E is equal to the ordinal number of the group in the periodic system. Thus for hydrogen and sodium $E = 1$, for carbon $E = 4$, for nitrogen and phosphorus $E = 5$, for oxygen and sulfur $E = 6$ and for chlorine $E = 7$.

We represent by e the total number of electrons in the shells of the atoms that combine to form a molecule. Let n be the number of octets formed

¹ G. N. Lewis, *THIS JOURNAL*, 38, 762 (1916), Langmuir, *Ibid.*, 41, 868, 1543 (1919); and *Proc. Nat. Acad. Sci.*, 5, 252 (1919)

from these electrons, and let p be the number of pairs of electrons which the octets share with one another. Since every pair of electrons thus shared reduces by two the number of electrons required to form the molecule, we are led to the "octet equation."

$$p = \frac{1}{2}(8n - e). \quad (1)$$

Each pair of electrons held in common by two octets corresponds to a covalence bond. In addition to bonds given by this equation there are those corresponding to pairs of electrons which hold hydrogen nuclei. Thus if H represents the number of hydrogen atoms in a molecule, the total number of covalence bonds v in the molecule is

$$v = p + H. \quad (2)$$

Let C , N , X and Cl represent, respectively, the numbers of carbon, nitrogen, oxygen and chlorine atoms in the molecule. Equation 1 thus gives

$$2p = 8(C + N + X + Cl) - (4C + 5N + 6X + 7Cl + H). \quad (3)$$

Simplifying and substituting in (2) we obtain

$$v = 4C + 3N + 2X + Cl + H. \quad (4)$$

We are also led to this equation if we calculate, by the ordinary valence theory, the total number of valence bonds in a molecule, assuming the valences to be, respectively, 4, 3, 2 and 1 for carbon, nitrogen, oxygen and chlorine. These valences are Abegg's countervalences and are each equal to $8 - E$. The factor 2 in the first term of Equation 4 results from the fact that in adding $4C$, $3N$, etc., we count each bond twice.

It is thus proved that any formula written in accordance with the ordinary valence theory will be in agreement with the octet theory, if we take the valence of hydrogen as unity and that of each other atom as $8 - E$. On the other hand, it is apparent that with valences other than $8 - E$, the ordinary valence theory leads to results different from those of the octet theory. It is the object of this paper to deal especially with cases of this kind.

As the first example, let us consider sodium chloride. For sodium $8 - E$, is 7 while the ordinary valence theory assumes a valence of unity. Applying the octet theory to sodium chloride, we place $e = 1 + 7 = 8$. The chlorine atom forms an octet, but we cannot reasonably assume that the sodium takes up 7 more electrons to complete an octet. Therefore, $n = 1$ and Equation 1 gives $p = 0$. The covalences of chlorine and sodium in this compound are thus each zero. But since $n = 1$ the chlorine atom must have a complete octet and must, therefore, be negatively charged. Similarly the sodium atom, having lost its extra electron, will be positively charged. The atoms are held together by electrostatic forces even without sharing electrons. This result is eminently satisfactory, for it explains at once why X-ray crystal analysis gives no evidence of molecules of sodium

state. This theory, however, does not indicate that sodium and chlorine ions should never be held together in pairs. The vapor of sodium chloride and solutions in non-ionizing solvents may well contain such pairs or molecules held together by the attraction of the ions, but even in this case the covalence would be zero. This conception seems more useful than one in which the valence is taken as the number of electrons transferred from one atom to the other. In the cases just considered it is so obvious that the two ions will tend to be drawn together by their electrostatic attraction, that we hardly need to use the conception of valence to describe the attraction.

This theory is in full accord with the theory of S. R. Milner¹ in which he argues that the ions in solutions of strong electrolytes are never associated into molecules, but that pairs of ions which are temporarily near together may act as if bound together electrostatically. This theory explains the failure of Ostwald's dilution law for strong electrolytes, and is quantitatively in agreement with the best experimental data on the conductivity of electrolytes. Almost identical theories of strong electrolytes have been developed recently by Bjerrum² and by Ghosh.³

As a second example let us consider the structure of ammonium chloride, a typical case in which the nitrogen is certainly not tervalent. Here $e = 16$, $n = 2$ and we obtain by Equation 1, $p = 0$. This means that the nitrogen and the chlorine octets do not hold electrons in common. If we consider that the 4 hydrogen nuclei are at first detached from the nitrogen and chlorine octets, then the nitrogen atom would have an excess of 3 negative charges, and the chlorine one negative charge. The hydrogen nuclei can distribute themselves between the two octets in such a way as to render them electrically neutral if 3 hydrogen nuclei are bound by 3 pairs of electrons in the nitrogen octet, while the fourth hydrogen nucleus goes to the chlorine. This gives a mixture of ammonia and hydrochloric acid gases and corresponds with the facts observed at high temperatures. On the other hand, since the more electronegative chlorine has the lesser tendency to share its electrons, the 4 hydrogen nuclei can attach themselves to the 4 pairs of electrons of the nitrogen octet forming a very symmetrical positive ion, while the chlorine remains as a negative ion. The ammonium ion and the chlorine ion thus have covalences of zero, but that of the nitrogen atom is 4. The structure of the ammonium ion is thus exactly like that of the methane molecule except for the difference in the charge on the nucleus. The relationship between the ammonium ion and methane is described by the term isosterism and this conception proves of value in correlating the similarity between the potassium and

¹ *Phil. Mag.*, 35, 214, 354 (1918)

the ammonium ions with that between argon and methane.¹ The same kind of reasoning can be used to explain the fact that the ammonium ion resembles the potassium ion more closely than it does the sodium ion. The sodium ion has a structure like the neon atom, but neon differs from methane much more than argon does, so we should expect the sodium ion to show similar differences from the ammonium ion. The low boiling points of argon and methane show that the external field around these molecules (or atoms) must be very small. There should then be no strong forces around the potassium and ammonium ions except those due to the electrostatic charge. The markedly different properties of the silver ion proves that in other cases there are forces of a different kind which are of importance in determining the properties. The silver ion is related to the palladium atom as the potassium ion is to argon, and the great difference between argon and palladium corresponds to the difference between the potassium and silver ions.

From the examples just cited it is clear that the octet theory applies satisfactorily even when the valence of atoms is not equal to $8 - E$. In these cases structural formulas are obtained quite different from those the ordinary valence theory of organic chemistry, but they are in perfect agreement with the properties of the compounds. It is true that Werner's theory leads to the correct constitution of ammonium compounds, but only by making a large number of assumptions of a quite different kind from those on which the organic structural formulas are based. The particular merit of the octet theory is that it gives a single simple theory which includes the extreme types of compounds represented by organic compounds, the alkali halides, and so-called complex compounds.

The octet theory as expressed by Equation 1 is, of course, not capable of showing distinctions between compounds of two elements which have the same number of electrons in their shells, as for example between nitrogen and phosphorus. However, as was pointed out in the previous paper, the theory can be supplemented by certain more or less empirical rules regarding the covalence of the various elements. The general study of compounds by the octet theory has shown the following covalences:

The inert gases, alkali and alkaline earth metals, zero. Carbon, 4 in all ordinary organic compounds, but in some cases the covalence may be 3 as for example in calcium carbide, triphenylmethyl sodium and many other triphenylmethyl derivatives. Nitrogen, usually 3, but 4 in most compounds where quinquivalent nitrogen has been assumed, and 2 in a few compounds. Oxygen, 1, 2 or sometimes 3 (in peroxides). Fluorine, zero or 1. Phosphorus, usually 4, sometimes 3 and rarely zero. Sulfur and chlorine may have any values from zero to 4.

According to the ordinary theory the valences of an element usually

increase by steps of two, thus nitrogen and phosphorus are supposed to have valences of 3 and 5; sulfur, 2, 4 and 6, chlorine, 1, 3, 5 and 7, etc. According to the octet theory, however, where the covalence is variable, its value increases by steps of one. The double steps of the ordinary theory are due to the fact that the total number of electrons, e , must be an even number according to Equation 2, so that where univalent elements are added two atoms must be added at a time. It is well known that oxygen atoms are added singly as in HNO_2 , HNO_3 , HClO , HClO_2 , HClO_3 and HClO_4 . The ordinary theory assumes that these are held by double bonds, while the octet theory shows that they are held by single pairs of electrons.

Tetravalent Nitrogen.

It was shown by Equation 4 that the structural formulas written according to the ordinary theory are always in accord with the octet theory when the valence of nitrogen is 3. Let us see, however, what light the octet theory throws on the stereoisomerism of nitrogen compounds.

In the previous paper reasons were given for believing that when the 8 electrons in an octet are not shared by other atoms they are normally arranged at the corners of a cube. A pair of electrons held in common by two atoms, however, acts as though it were located at a point. When an atom has a covalence of 4 the 8 electrons in its octet are, therefore, drawn together into 4 pairs which arrange themselves symmetrically at

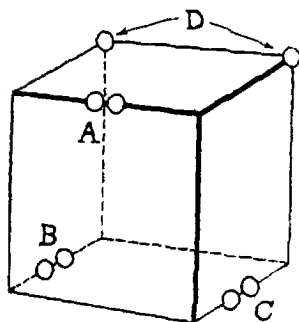


Fig. 1

the corners of a regular tetrahedron. As Lewis already pointed out, stereoisomerism of carbon compounds is thus fully explained. The same reasoning applies to atoms of nitrogen, phosphorus, sulfur, etc., whenever these atoms are tetravalent, so that stereoisomers are obtained under the same structural conditions as with carbon compounds. The experimental facts are in full accord with this conclusion.

When only 3 pairs of electrons in an octet are shared we should expect an arrangement like that shown diagrammatically in Fig. 1.

The 3 pairs of electrons, A, B and C, which correspond to the 3 covalence bonds are arranged in space approximately like 3 of the corners of a regular tetrahedron. The fourth corner corresponds to the unshared pair, D. This arrangement of the 3 bonds in space agrees exactly with Hantzsch and Werner's¹ theory which has so well explained the isomerism of aldoximes, ketoximes, hydrazones, osazones, diazo compounds, etc. Neogi's

¹ Ber., 23, 11 (1890)

recent theory¹ assumes an identical arrangement of the valence bonds. For a full discussion of the evidence in favor of this arrangement Neogi's paper should be consulted.

The absence of isomers among amines containing 3 different groups is not inconsistent with this theory, for it can be satisfactorily explained by a mobility of the groups caused by the presence of the unshared pair of electrons at D. Thus, in a compound $\text{NR}_1\text{R}_2\text{R}_3$, each of the 3 alkyl groups holds a pair of electrons in common with the nitrogen atom, but the nitrogen atom has another pair of electrons (D in Fig. 1) which is not shared. We may assume that the alkyl groups are able to shift into the unoccupied position while the pair of electrons has mobility enough to allow it to occupy the position just vacated by the alkyl group. This could occur without the alkyl radical becoming detached from the nitrogen atom at any time. A similar mobility would not exist if all 4 pairs of electrons were shared. Stereoisomers among compounds of tervalent nitrogen are observed only when the nitrogen is held by a double bond, that is, when two of its pairs of electrons, as for example B and C in Fig. 1, are shared by a single other atom. Such a behavior seems quite reasonable on the basis of this structure. With the double covalence bond it is natural that new constraints should be called into existence in the atom and that the mobility of its other electrons should be decreased.

Quadricovalent Nitrogen, Etc.

The structure of tetramethyl ammonium hydroxide, $(\text{CH}_3)_4\text{NOH}$ is found by placing $e = 40$; $n = 6$ which gives $p = 4$. The nitrogen is thus quadricovalent (as in the ammonium ion) and the hydroxyl ion exists as a negative ion which does not share electrons with the ammonium radical. It is thus completely ionized in solution and is, therefore, a strong base. Of course any other negative ion can take the place of the hydroxyl ion.

In applying the octet theory to the structure of organic compounds it is usually convenient to consider the different parts of molecules separately. We can accomplish this by letting R, R', etc., represent univalent radicals and assuming that for each radical $E = 7$ and $n = 1$. For example, the radical C_3H_7 in a molecule really contributes 19 electrons to e and 3 octets to n . If we replace this by R we add only 7 electrons to e instead of 19 and one octet to n instead of 3. This decreases n in Equation 2 by 2 units and decreases e by 12 units. The result is that the value of p found by the equation is decreased by 2 units, i. e., $\frac{1}{2}(16 - 12)$. But since 2 pairs of electrons must be shared between octets in C_3H_7 while none are needed for R, it is evident that we have not affected the value of p for the remainder of the molecule by substituting R for C_3H_7 . This reasoning will be found to hold whenever R represents any univalent radical. For a divalent radical we can place $E = 6$, $n = 1$.

According to this theory the substituted ammonium compounds should show isomerism exactly like that of carbon compounds, since the nitrogen is quadricovalent. This is in full accord with Werner's theory and with all the experimental data. Neogi¹ raises an objection to Werner's theory on the grounds that the latter "has postulated the existence of as many as three kinds of valence, *viz.*, (1) principal, (2) subsidiary valences of nitrogen, and (3) residual valence of the ammonium group." It is seen that the present theory reaches a conclusion essentially similar to Werner's without making any additional assumptions regarding valence. The octet theory thus removes the objections that have been raised against Werner's theory. Neogi's own assumption of a tetrahedral nitrogen atom is, of course, in full agreement with the octet theory, but his assumption of a fifth bond "attached to the nitrogen by principal valences, though four of them are in the inner zone and the fifth is in the outer zone" is entirely unnecessary and introduces needless complication. Neogi states that "there is no escape from acknowledging the pentavalence of nitrogen as in the amine-oxides $O \cdot NR_2R_3$." The octet theory gives for the amine-oxides $e = 32$, $n = 5$ and $p = 4$. Thus the nitrogen is quadricovalent and it is entirely unnecessary to assume quinquevalent nitrogen. The octet theory thus greatly simplifies our conception of the structure of compounds of this type. The amine oxides should, of course, exist in two optically isomeric forms whenever the 3 substituted radicals are different, just as in other cases of quadricovalent nitrogen. Neogi by arbitrary assumptions explains the isomerism of these oxides, but states that none of the other theories of the stereoisomerism of nitrogen compound is able to do so.

The isomeric compounds $(Me_3NOR)OR_1$ and $(Me_3NOR_1)OR$ prepared by Meisenheimer² are satisfactorily explained by the octet theory. One of the OR radicals exists as a negative ion as in the alcoholates, while the other shares a pair of electrons with the nitrogen atom.

One fundamental objection to Neogi's theory is that it gives no adequate reason why only radicals capable of forming *negative* ions can be held by the fifth bond.³

The octet theory throws a great deal of light on the properties of ammonium compounds. Since in typical ammonium salts the NH_4 group exists as an ion, the physical properties should resemble potassium salts for the reasons already given. The close relationship between the solubilities, crystalline forms, etc., of ammonium and potassium salts is in

¹ *Loc. cit.*, p. 623

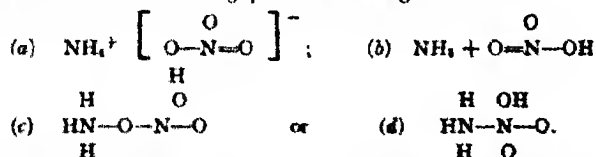
² *Ann.*, 397, 273 (1913)

³ The absence of optical isomers of the substituted pyridinium and quinolinium compounds referred to by Neogi on p. 638 of his paper is undoubtedly to be explained by an effect in the pyridine ring similar to that which prevents the occurrence of two

fact very striking, but in certain other respects such as vapor pressures, melting points, etc., there are often striking differences. Ammonium chloride sublimes without melting at about 340° at atmospheric pressure, while the corresponding potassium salt melts at 772° , and boils only at very much higher temperatures. It is probable that this difference is due to the dissociation into ammonia and hydrogen chloride although this simple assumption does not wholly account for the facts since perfectly dry ammonium chloride is said to vaporize without dissociation. However, the total vapor pressure at a given temperature has been found to be the same whether or not the vapor is dissociated.¹ This seemingly incomprehensible result probably indicates that something closely related to dissociation does occur even when the vapor density corresponds to that of ammonium chloride, and that in any case the so-called "undissociated" vapor probably has molecules of a quite different structure from those that would be obtained from potassium chloride. It would seem that a study of the dielectric constants of the "dissociated" and "undissociated" vapors and possibly their electric conductivities or ionizing potentials might clear up these puzzling questions.

The failure to obtain the ammonium halides in the molten condition is what is to be expected by the octet theory.² There are, however, other ammonium salts which melt at rather low temperatures compared to the corresponding potassium salts. As examples let us consider ammonium nitrate which melts at 166° while potassium nitrate melts at 337° , and ammonium trinitride, NH_4N_3 , which melts at 110° .

Applying the octet equation to ammonium nitrate we find $p = 4$. This leads to the following possible arrangements:



¹ Abegg, *Z. physik. Chem.*, 61, 455 (1908), and subsequent papers by van Laar, Wegscheider and Scheffer.

² With the assistance of Miss Katharine Blodgett, I have found that pure ammonium chloride, sealed up in a small, heavy-walled Pyrex glass tube and heated, melts to a clear liquid at about 550° . By plotting the logarithms of the vapor pressures, measured by Smith and Calvert, *THIS JOURNAL*, 36, 1373 (1914), against the reciprocals of the corresponding absolute temperatures a straight line was obtained. Extrapolation along this line gives the vapor pressure of ammonium chloride at 550° as 66 atmospheres. The ratio between the melting point of ammonium chloride (823° K.) and that of potassium chloride (1045° K.) is not greatly different from the ratio between the melting point of ammonium hydrogen sulfate (413° K.) and that of potassium hydrogen sulfate (473° K.). The lower melting point of the ammonium salts and their somewhat greater solubilities are probably to be accounted for by the tetrahedral shape of the ammonium ion (like that of the methane molecule) as compared to the octahedral shape of the potassium ion.

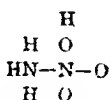
Structure (a) corresponds to the salt type; this should have a melting point comparable with that of potassium nitrate.

Structure (b) corresponds to a possible dissociation into nitric acid and ammonia.

Structures (c) and (d) suggested by the octet theory are quite inconsistent with the ordinary valence theory. The melting of anhydrous ammonium nitrate perhaps depends, however, upon the formation of one or both of these tautomeric products.

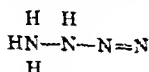
Upon heating, (c) should give $2\text{H}_2\text{O} + \text{N} \equiv \text{N}$, while (d) should give $2\text{H}_2\text{O} + \text{N}=\text{N}=\text{O}$. These constitutions thus explain the formation of nitrous oxide.

We shall see from data to be given further on that there is good evidence that nitrous oxide is represented by the structure $\text{N} \equiv \text{N}-\text{O}$. Therefore, molten ammonium nitrate probably contains some molecules having the structure



It is to be expected that molecules of this type have relatively weak external fields of force as compared to $\text{NH}_4^+ \text{NO}_3^-$.

In a similar way the melting of NH_4N_3 at 110° is, perhaps, to be ascribed to the formation of molecules of the structure



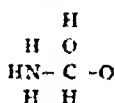
According to the above hypothesis the difference between the melting points of the ammonium salts and the corresponding potassium salts is dependent on the presence of double bonds in the anion of the acid. Ammonium sulfate has an anion in which there are no double bonds, and the central atom has a covalence of 4. It is, therefore, not possible for the ammonia group to attach itself to the sulfate ion in the same manner as with the nitrate ion. Therefore, we should expect ammonium sulfate to have a melting point only a little lower than that of potassium sulfate (1072°). Now most tables of physical constants and handbooks like Abegg's give the melting point of ammonium sulfate as 140° . These statements seemed so radically inconsistent with the octet theory that I was led to test the data by experiment. It was found that ammonium sulfate remained practically unchanged until heated to about 280° and it then decomposed, giving off ammonia and yielding fused ammonium hydrogen sulfate. Subsequently I found that Reik¹ had already observed, that ammonium sulfate decomposes without melting, and that it is the acid sulfate NH_4HSO_4 .

¹ *Monatsh.*, 23, 1033 (1902).

which melts at 140° . This is not greatly different from the melting point of potassium hydrogen sulfate, so that the low melting point is not inconsistent with the octet theory. The fused ammonium hydrogen sulfate is a very good electrolytic conductor and probably consists wholly of ions of NH_4^+ and HSO_4^- .

The relatively low melting point of ammonium nitrate and the infusibility of the sulfate thus support the conclusion from the octet theory that the nitrate ion has a double bond, while in the sulfate ion the 4 oxygen atoms are held to the sulfur by single bonds. The ordinary valence theory on the other hand is not capable of showing such a distinction, for it gives double bonds for both anions.

Ammonium formate, NH_4CHO_2 , melts at 115° , and at 180° decomposes into formamide and water. Although this melting point is not greatly below that of the potassium salt (150°) it is possible that the melt contains a proportion of molecules having the structure



in which one of the oxygen atoms is univalent. It is apparent that water can be readily split off from this molecule yielding formamide, H_2NCHO .

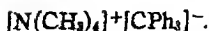
Schlenk and Holtz¹ have prepared a compound, triphenylmethyltetramethyl ammonium, in which 5 hydrocarbon residues are supposed to be attached to a single nitrogen atom, and which would thus furnish direct evidence of quinevalent nitrogen. The compound is described as forming a "red shimmering crystalline mass with blue metallic luster," which is immediately decomposed by water yielding triphenylmethane and tetramethyl ammonium hydroxide. It is formed by the action of triphenylmethyl sodium on dry tetramethyl ammonium chloride in solution in ether.

Applying the octet theory to triphenylmethyl sodium by placing $e = 26$, $n = 4$, we find $p = 3$. Each of the 3 phenyl radicals shares a pair of electrons with the carbon atom, but the sodium atom shares no electrons with the organic radical. The constitution is, therefore,



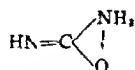
The central carbon atom has a covalence of 3, but has its complete octet. This formula is in full accord with the unusual properties of this substance and explains, for example, its strong color and its reaction with ammonia to form triphenylmethane and sodium amide, Na^+NH_2^- . It is thus evident that the triphenylmethyltetramethyl ammonium which is derived from the triphenylmethyl sodium should have the constitution

¹ *Ber. 40, 699 (1907)*



This substance should thus be a salt whose ions are held together by electrostatic attraction. The covalence of the nitrogen is 4 while that of the central carbon atom in the anion is 3. It is stated by Schlenk and Holtz that a solution of this substance in pyridine conducts the electric current, so there can be no question of its salt-like character.

The structure



has been proposed for carbamide by E. A. Werner,¹ while W. A. Noyes and R. S. Potter,² in accordance with the views of others, have assumed the formula (a)



for certain amino acids. In the case of compounds of this second type the octet theory gives $p = 5$ which makes it impossible to place a covalence bond between the oxygen and the nitrogen. However, the formula may be written (b)



in which it is evident that the normally electrically neutral ammonia must become positively charged when it shares a pair of electrons with the carbon atom of the R group. Similarly the oxygen atom must be negatively charged because it has lost the positive charge which the NH_2 group has acquired (in being converted to NH_3). Under these conditions, in the absence of an ionizing solvent, it is natural that the positive and negative groups should be held together electrostatically as indicated by the dotted line in Formula b. This formula thus represents clearly the properties of the compound and is fully in accord with the experimental results of Noyes and Potter. Since in this case the oxygen and nitrogen cannot hold a pair of electrons in common, it seems desirable not to connect them by a valence bond in the formula.

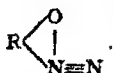
Similar considerations apply to the structure of carbamide.

It is interesting that in the analogous case of the so-called diazophenols studied by Klemenc³ the octet theory indicates the possibility of a true ring formula closed by covalence bonds. Klemenc has given evidence for the formula

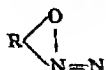
¹ *Chem. Soc. Trans.*, 107, 715 (1915).

² *THIS JOURNAL*, 37, 189 (1915).

³ *Ber.*, 47, 1407 (1914).



The octet theory gives $p = 5$, which leads to the modification



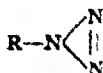
The covalence of one of the nitrogen atoms is 4, while that of the other is two, but there is no development of free charges as in the case of the amino acids

The formula given for diphenylene-diazomethane, $(\text{C}_6\text{H}_5)_2\text{C}=\text{N}=\text{N}$,¹ is consistent with the octet theory if the triple bond is replaced by a double bond. In general, it is, perhaps, probable that $>\text{C}=\text{N}=\text{N}$ represents the diazo group rather than



The diazonium compounds may have either the structure $(\text{R}-\text{N} \equiv \text{N})^+ \text{OH}^-$ or $\text{R}-\text{N}=\text{N}-\text{OH}$. This tautomerism explains the fact that in some cases these compounds exhibit acid as well as alkaline properties, while the unusual triple bond explains the explosive properties. The positive charge is probably not localized on either nitrogen atom but the $-\text{N} \equiv \text{N}$ group as a whole is positive because it shares its electrons with the R group.

The triazo compounds RN_3 may have the structure $\text{R}-\text{N}=\text{N}=\text{N}$ rather than

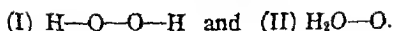


Hydronitric acid is then $\text{H}-\text{N}=\text{N}=\text{N}$ and the nitride ion has the very symmetrical structure $\text{N}=\text{N}=\text{N}$. This structure is in full accord with the experimental facts referred to by Turrentine² in his discussion of the structure of hydronitric acid, from which he concludes that the structure should be $\text{H}-\text{N}=\text{N}=\text{N}$.

The properties of hydroxylamine indicate that this substance exists in two tautomeric forms³ which may be represented according to the octet theory by (I) $\text{H}_2\text{N}-\text{OH}$; and (II) $\text{H}_2\text{N}-\text{O}$; the second of these formulas corresponding to that of the amine oxides already considered. The relationship of this compound to hydrogen peroxide discussed by L. W. Jones is thus made particularly clear, for this latter substance also exists in two tautomeric forms.

¹ Staudinger and Gaule, *Ber.*, 49, 1961 (1916)

² *This Journal*, 36, 23, (1914)



The form II contains in both cases univalent oxygen atoms and these formulas thus account directly for the oxidizing properties of these substances.

Hydrogen ions (or nuclei) are able to attach themselves to the free pair of electrons of the nitrogen octet in H_2NOH to form an ion H_4NOH^+ . But the tendency to form this ion is weaker than that by which the ammonium ion is formed from ammonia and the hydrogen ion because the larger charge on the nucleus of the oxygen atom displaces the electrons of the nitrogen octet towards the oxygen atom, while the nucleus of the nitrogen atom is displaced in the opposite direction. The presence of the hydroxyl group thus causes a decrease in the force with which the octet of the nitrogen atom holds hydrogen nuclei. There is no necessity for assuming polar valence.

For these reasons hydroxylamine has much weaker basic properties than ammonia. Notwithstanding this, the salts of hydroxylamine such as NH_2OHCl are completely ionized whether in solution or in the solid state. The reason that ammonia in aqueous solution is a weak base as compared to potassium hydroxide is that only a small fraction of the ammonia molecules combines with hydrogen ions from the water forming ammonium ions and thus liberating hydroxyl ions. The weakness of ammonia as a base is not to be looked upon as due to a lack of ionization of ammonium hydroxide, for this substance, according to the octet theory, can only exist in the completely ionized condition.

Acids, Bases and Salts.

We have just seen why such substances as ammonia, hydroxylamine, etc., behave as weak bases. The octet theory indicates, however, that potassium hydroxide, barium hydroxide, and tetramethyl ammonium hydroxide can exist only in the ionized condition. That is, even in the solid state, potassium hydroxide consists of potassium ions and hydroxyl ions held together by their electrostatic attraction. In tetramethylammonium hydroxide, the 4 methyl groups share all four pairs of electrons of the nitrogen octet, so that there are no pairs of electrons by which the oxygen could be held. Here again the substance is completely ionized. It follows, therefore, directly that this substance must be as strong a base as potassium hydroxide. For the same reason the compounds $\text{P}(\text{CH}_3)_3\text{OH}$ and $\text{S}(\text{CH}_3)_2\text{OH}$ are strong bases.

In the hydrochloric acid molecule the hydrogen nucleus shares a pair of electrons with the chlorine atom. Anhydrous liquid hydrogen chloride is, therefore, a non-conductor of electricity since there are no free ions. But when this substance is brought into contact with water, the hydrogen

the octets of the water molecules than to the chlorine atoms, since the nuclei of the oxygen atoms have smaller positive charges than those of the chlorine atoms. The result is that the hydrogen nuclei become hydrated hydrogen ions, and the chlorine ions remain in solution. This explanation of the separation of the hydrochloric acid molecule into ions is not essentially different from that which attributes the effect to the high dielectric constant of the water.

If we consider another substance such as hydrogen sulfide, it is clear that the tendency for the hydrogen nuclei to separate from the octet to which they were originally attached may be very much less. The smaller positive charge on the kernel of the sulfur atom as compared with that of the chlorine atom causes the hydrogen nucleus to be much more firmly held. Another way of expressing this relationship is to say that chlorine readily assumes a form in which it has the covalence of zero, while sulfur has a greater tendency to be divalent than univalent. Ammonia, as we have seen, acts as a base rather than as an acid. That it thus tends to take up a fourth hydrogen nucleus instead of giving up those that it has, is due to the smaller positive charge on its kernel, and to the fact that the 4 nuclei enable it to assume a particularly stable form.

For these same reasons methane acts neither as an acid nor as a base. The small charge on the kernel allows the 4 hydrogen nuclei to be very firmly held by the 4 pairs of electrons so that acid properties are absent. There can be no basic properties because the molecule cannot take up any more hydrogen nuclei, all 4 pairs of electrons in the octet already being occupied.

From this viewpoint, acids are substances from whose molecules hydrogen nuclei are readily detached, while bases are substances whose molecules can easily take up hydrogen nuclei. The more easily the hydrogen nuclei are given up, the stronger the acid which results: the greater the tendency to take up hydrogen nuclei the stronger the base. Typical salts, on the other hand, are completely ionized even in the solid state, and are, of course, completely ionized in solution. The variation in electric conductivities, osmotic pressures, etc., of salt solutions is quantitatively explained by Milner and Ghosh as due to the constraints caused by the electric charges which tend to produce a uniform distribution of positive and negative ions, whereas if the particles were uncharged there would be a random distribution.

There are certain substances usually regarded as salts, whose aqueous solutions show relatively little conductivity. Mercuric chloride and cyanide, cadmium iodide, etc., are typical examples of this kind. Mercuric and cadmium ions unquestionably have strong external fields of force in addition to the forces caused by their electric charges. Accord-

strontium differ from atoms of argon and krypton only in their electric charges. Since the stray forces around the atoms of the inert gases are very small, it follows then that the properties of the ions of calcium, strontium, etc., are determined almost wholly by the charges on the ions. But cadmium and mercuric ions have structures like atoms of palladium and platinum, respectively, so that, as in these latter atoms, it must be assumed that there are strong fields of force around the ions in addition to those caused by their charges. It is, therefore, probable that in mercuric chloride, the atoms exist as ions, but that these ions do not separate from each other when the substance goes into solution. The existence of the various organic compounds and complex ions of mercury furnishes abundant confirmation of this theory of strong secondary valence forces about atoms of mercury and other related elements.

Isomerism of Cyanates, Cyanides, Nitrides, Etc.

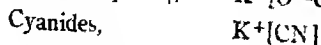
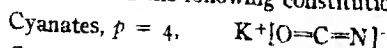
It is well known that organic cyanates, cyanides and nitrites, exist in two isomeric forms. According to the octet theory the constitutions of these substances are as follows

	p	Normal	Iso
Cyanates	5	$R-O-C \equiv N$ or $R-O-C \equiv N$	$R-N \equiv C=O$
Cyanides or nitriles..	4	$R-C \equiv N$	$R-(NC)$
Nitrites or nitro-compounds..	4	$R-O-N=O$	$R-N \begin{array}{l} \diagup O \\ \diagdown \end{array}$

The second column gives p the number of pairs of electrons held in common between the atoms as calculated from the octet equation.

In the isonitriles the nitrogen and carbon kernels are probably contained within a single octet as in the cyanogen ion, and in the nitrogen and carbon monoxide molecules.

If we apply the octet theory to the structure of inorganic cyanates, cyanides and nitrites we find the following constitutions:



The theory thus indicates that these substances differ essentially from the corresponding organic compounds in that the atoms of the metal are not attached to definite atoms of the acid radical. It is, therefore, evident from the octet theory that these substances should not exist in two isomeric modifications, and that the structures of these inorganic compounds do not correspond to either the normal or to the iso organic derivations. These conclusions are in full accord with the facts.

Free cyanic, hydrocyanic and nitrous acids exist in only one form each.

pletely ionized condition. These facts simply illustrate again the mobility of the hydrogen nucleus when bound by atoms having a covalence less than 4. We may, therefore, consider that in these free acids both the modifications observed among the organic derivatives exist together in tautomeric equilibrium.

Phosphonium, Arsonium, Sulfonium and Oxonium Compounds.

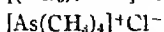
Whereas the ammonia molecule has a relatively strong tendency to take up a hydrogen nucleus to form the ammonium ion, the corresponding tendency of phosphine to take up the hydrogen nucleus is very weak. This decrease in the affinity for hydrogen nuclei in passing from nitrogen to phosphorus, corresponds to the fact that hydrochloric acid is a stronger acid than hydrofluoric and hydrogen sulfide has stronger acid properties than water.

The introduction of a chlorine atom into acetic acid to form chloroacetic acid, according to the viewpoint of G. N. Lewis, displaces all the electrons towards the chlorine atom. This decreases the forces holding the hydrogen nucleus in the hydroxyl group and by allowing this hydrogen ion to be more readily detached, makes the chloroacetic acid a stronger acid than acetic. A replacement of the same hydrogen atoms by alkyl radicals allows the electrons to shift towards the hydroxyl group, increasing the forces holding the hydrogen nucleus and making the acid weaker. In a similar way the replacement of the hydrogen atoms in phosphine increases the tendency for the molecule to take up hydrogen nuclei and strengthens the basic properties. Thus trimethyl-phosphine has distinctly basic properties, although these are much less than those of trimethyl-amine.

On the other hand the phosphonium bases or quaternary compounds such as tetramethyl-phosphonium hydroxide are exceedingly strong bases quite comparable with potassium hydroxide and tetramethyl-ammonium hydroxide. In these compounds, just as in ordinary ammonium salts the central atom must be quadricovalent and the negative radical thus exists as an ion which does not share electrons with the positive radical.

The basic properties of the arsine derivatives are still less marked. Thus even tertiary arsines do not have basic properties. On the other hand, as is to be expected, the quaternary arsonium bases are about as strongly basic as potassium hydroxide and the other quaternary bases.

As distinguished from the corresponding ammonium compounds, it is possible to replace the hydrogen of alkyl substituted phosphines and especially arsines by chlorine. All such compounds whose formulas can be written by giving arsenic a valence of 3 are of course in agreement with the octet theory. The structures of the arsenic chlorides are



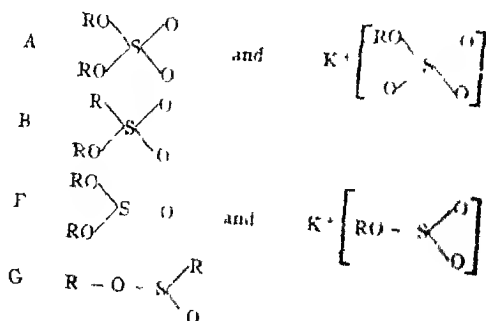
In the corresponding oxides $(\text{CH}_3)_3\text{AsO}(\text{OH})_2$, $(\text{CH}_3)_2\text{AsO}(\text{OH})$ and $(\text{CH}_3)_3\text{AsO}$, all 4 radicals are attached directly to the quadricovalent arsenic atom, so that these compounds are not salt-like in character.

For sulfonium compounds such as $(\text{CH}_3)_3\text{SI}$ we place $c = 34$, $n = 5$ and find $p = 3$. The constitution is thus $[\text{S}(\text{CH}_3)_3]^+\text{I}^-$, where the sulfur atom is tervalent. The corresponding base $[\text{S}(\text{CH}_3)_3]^+\text{OH}^-$ is, of course, completely ionized and is, therefore, comparable to potassium hydroxide.

In compounds with oxygen and organic radicals, sulfur takes, with almost equal ease, valences of 3 or 4. This leads to a great variety of organic compounds. The following table gives a list of such types of compounds together with the constitutions as derived from the octet theory

ORGANIC SULFUR OXYGEN COMPOUNDS ETC			
	Quadricovalent sulfur		Tervalent sulfur
A Sulfates	$(\text{K}^+)_2 \left[\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \right]$	F Sulfites	$(\text{K}^+)_2 \left[\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \right]^-$
B Sulfonates	$\text{K}^+ \left[\begin{array}{c} \text{R} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \right]$	G Sulfates	$\text{K}^+ \left[\begin{array}{c} \text{R} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \right]^-$
C. Sulfones	$\left[\begin{array}{c} \text{R} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{O} \end{array} \right]$	H Dialkyl sulfoxides	$\text{P} \begin{array}{c} \text{R} \\ \diagdown \\ \text{S} \\ \diagup \\ \text{O} \end{array}$
D. Trialkyl sulfine iodide	$\left[\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array} \right]^+ \text{I}^-$	I Sulfonium compounds	$\left[\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array} \right]^+ \text{I}^-$
E Tetraalkyl sulfonium iodide	$\left[\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array} \right]^{++} (\text{I}^-)_2$		

In addition to these there are, of course, various possible esters of the acids, such, as

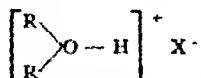


where the letters A, B, F and G refer to the corresponding substances in the preceding table.

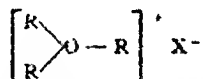
The compounds given under E in the first table, namely, compounds of the type $[S(CH_3)_4]^{++}I_2^-$ have, I believe, not been isolated. But a closely corresponding cyclic compound trimethylene-dimethyl-sulfonium diiodide $[CH_2 \cdot CH_2 \cdot CH_2 \cdot S(CH_3)_2]^{++}I_2^-$ has been prepared and studied by

Grishkevich-Trokhimovskii.¹ He found that both iodine atoms are equally ionized and are precipitated by silver nitrate.

For oxonium compounds such as those of the type $R_2O \cdot HX$ we place $e = 28$; $n = 4$ and find $p = 2$. The hydrogen nucleus can, however, attach itself to one of the unoccupied pairs of electrons of the oxygen atom so we arrive at the structure



For compounds of the $R_2O \cdot RX$ type we place $e = 34$; $n = 5$ and find $p = 3$, whence the constitution is



corresponding exactly to the sulfonium compounds.

The constitutions of the phosphonium, sulfonium, oxonium, compounds, etc., arrived at by the octet theory correspond to those found by Werner's theory. The octet theory, however, has the advantage that it does not require special assumptions regarding valence for compounds of each of these types.

Summary.

The octet theory of valence which has been described in previous papers is here applied particularly to organic nitrogen compounds, although the general application of the theory to inorganic nitrogen compounds and to salts is discussed.

The numbers of available electrons in the outside shell of any atom is usually given by the ordinal number of the column of the periodic table in which the element is found. This number, which we may represent by E , corresponds to the maximum positive valence of the ordinary valence theory and is one for sodium, 4 for carbon, 5 for nitrogen, 6 for oxygen, and 7 for chlorine.

It is readily proved that the octet theory is entirely in agreement with the ordinary valence theory whenever the ordinary formulas are based on valences of unity for hydrogen and $8 - E$ for each other element. Thus the ordinary formulas agree with those of the octet theory whenever we

¹ *J. Russ. Phys. Chem. Soc.*, 48, 880 (1916).

take the following valences: hydrogen, one; carbon, 4; nitrogen and phosphorus, 3; oxygen and sulfur, 2; and chlorine, bromine, etc., one. On the other hand all formulas in which valences different from these have been used require modification according to the octet theory.

The octet theory is applied, among others, to the following compounds, whose formulas require modification.

Sodium chloride Na^+Cl^- (the covalence of both atoms is zero),

Ammonium chloride $\left[\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{N} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array} \right]^+ \text{Cl}^-$ (the nitrogen is quadricovalent).

Triphenylmethyltetramethyl ammonium $[\text{N}(\text{CH}_3)_4]^+[\text{CPh}_3]^-$ (the nitrogen is quadricovalent while the central carbon atom in the anion is tercovalent).

Diazophenol $\text{R} \begin{array}{c} \diagup \text{O} \\ | \\ \text{N} = \text{N} \end{array}$

Diazonium compounds $[\text{R}-\text{N}\equiv\text{N}]^+\text{OH}^-$ or $\text{R}-\text{N}\equiv\text{NOH}$

Triazo-compounds $\text{R}-\text{N}\equiv\text{N}=\text{N}$

Hydroxylamine H_2NOH or $\text{H}_2\text{N}-\text{O}$, etc

According to this theory all salts are completely ionized even before they are brought into solution. This conclusion is, however, in accord with recent work of Milner, Ghosh and others. It explains why there are weak acids and weak bases but no weak salts

The known cases of isomerism, including stereoisomerism, of nitrogen, phosphorus and sulfur compounds are in full accord with the octet theory.

The fact that organic cyanates, cyanides and nitrites exist in two isomeric forms, while the corresponding inorganic salts exist in only one form, is explained, since the multicovalent atoms of the metals in the inorganic compounds are not attached to definite atoms of the acid radicals.

The available data on phosphonium, arsonium, sulfonium and oxonium compounds are in full accord with the octet theory, which gives for these compounds constitutions closely resembling those previously given by Werner.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE TAKAMINE LABORATORY.]

A METHOD OF TESTING THE AMYLOLYTIC ACTION OF THE DIASTASE OF *ASPERGILLUS ORYZAE*.

BY SELMAN A. WAKSMAN.

Received October 18, 1919.

In the action of diastatic enzymes upon starch, we differentiate between the amylolytic (amylolytic, liquefying) power and the saccharogenic (saccharifying) power. We usually speak of diastase as one enzyme, but we might consider, more properly, this enzyme to consist of two classes of enzymes, one of which hydrolyzes the starch to soluble starch, dextrins and maltose (amylase) and the other hydrolyzes the maltose into dextrose (maltase), but, since both classes of enzymes are usually found in the same mixture and were not as yet separated from one another, they are looked upon as one group of enzymes or even one enzyme. But the very fact that the diastatic enzymes obtained from different sources do not reduce the starch alike to the same end products, as will be pointed out later, would lead us to doubt the validity of many comparative studies of different enzyme preparations based upon the determination of the same end product. Some diastases, notably the malt preparations, although acting readily on starch (strong amylolytic power) and hydrolyzing it to dextrins and finally to maltose, do not hydrolyze the latter to any large extent into dextrose, while diastase obtained from *Aspergillus Oryzae* (taka-diastase), in acting upon starch, hydrolyzes it into dextrins, then to sugars and results in a mixture consisting of glucose and maltose, free from any dextrins.

A review of the various investigations on the action of diastase reveals the fact that, in most of these, the saccharogenic power of the enzymes, rather than the amylolytic, was measured, for various reasons. First of all, in determining the saccharogenic power, we are dealing with the end products of the action of the enzyme upon starch, namely the sugars, which are measured readily by various methods. While in the study of amylolytic power, we have to measure either the amount of starch that has been hydrolyzed and this is not very satisfactory; or to determine the disappearance of the starch reaction with iodine, which also is not entirely satisfactory, since we have to differentiate then between the starch paste, soluble starch, and even higher dextrins which result in the first step of the hydrolysis of starch. The other reason for measuring the sugar production by enzymes from starch is due to the fact that the action of diastase was directed towards producing sugars from starch both in the feeding experiments and the production of beverages, therefore, it was natural to measure the saccharogenic rather than the amylolytic power.

The investigations presented here were conducted for the purpose of

finding the best methods suitable for the measurement of the action of diastatic enzymes used in the textile industry for the purification of the fabrics from starches and starch derivatives (process of desizing). Naturally, under these conditions, emphasis should be laid on the amylolytic power of the enzymes rather than on the saccharogenic power, since in the textile industry we are concerned with the first step of the action of the enzymes upon starch, namely, the dissolving of the starch or bringing it to such a state where it would dissolve in water rapidly and could be washed out, while the rapidity of sugar production is of little interest.¹

Historical.

A complete review of the different methods used in the study of diastatic action upon starch is found in the series of papers published by Sherman and associates.² Briefly stated, the methods for measuring the saccharogenic action consist in measuring the amount of sugar produced by determining the reduction of Fehling's solution, these methods are collectively designated by Sherman and associates as "copper" methods. The amylolytic (amylolastic) or liquefaction methods aim to measure the power of the enzymes to convert a definite amount of starch into products which give no longer the characteristic reaction with iodine and are designated by Sherman and associates as "iodine" methods. The only criticism to be submitted here on the so-called "saccharogenic" or "saccharification" methods is, as was pointed out above, the entire lack of differentiation between maltose and dextrose. This has been recognized by Davis and Daish,³ who, utilizing the fact that "taka-diastase" converts starch only into maltose and dextrose free from dextrin, used this method for the determination of starch in plant tissues, both the maltose and dextrose were evaluated by measuring the reducing power of the starch digest and the rotating power. Knowing the rotatory and reducing powers of the two sugars and of the unknown starch digest, we can easily figure out the quantity of maltose and dextrose present, and, therefore, of starch digested.

The iodine methods consist in testing the disappearance of the blue color (indicating disappearance of starch) or of any color (disappearance of starch and certain dextrans), upon adding a drop or two of the mixture of a standard starch solution and enzyme to a dilute solution of iodine (see Johnson,⁴ Wohlgenuth,⁵ Sherman⁶).

¹ May, *J. Soc. Dyers and Colourists*, 27, 88 (1912).

² *THIS JOURNAL*, 32, 1073, 1087, 33, 1195 (1911); 34, 1104 (1912); 35, 1617, 1784, 1790 (1913); 37, 623, 643, 1305 (1915); 38, 1638, 1877, 1885 (1916); 41, 231 (1919).

³ *J. Agr. Sci.*, 6, 152 (1914)

⁴ *THIS JOURNAL*, 30, 798 (1908)

⁵ *Biochem. Z.*, 1, 9 (1908)

⁶ *THIS JOURNAL*, 32, 1073 (1910)

Experimental.

In this study only the liquefaction of the starch is taken up; the methods of Johnson, Sherman and associates, and others based upon the reduction of the starch by the enzyme to substances no longer giving any color with iodine were not suitable for the purpose which we here have in view, since these methods measure not the first step in the liquefaction of the starch but the total disappearance of the starches and dextrins; the difference between the saccharogenic methods and these iodine methods consist in the fact that in the first case the sugars are measured directly, while in the second the conversion of the starch into sugars is measured. The only other method, which actually measures the liquefaction of starch is that of Wohlgenuth and its various modifications, in which the disappearance of the blue color with iodine is taken as an end-point, but not a total absence of color with iodine. This method, based upon a degree of color, is subject to various criticisms, since it will vary in the hands of different investigators.

The method used here is based upon the disappearance of the starch (the so-called "raw starch" was used) in the solution, without considering the fact of just how much of the starch has been hydrolyzed to dextrins and how much into sugars, thus measuring as nearly as possible the first step in the hydrolysis of starch.

Since, as Sherman and associates¹ have recently shown, potato starch is obtained almost pure by washing with water only and is as readily acted upon in the water washed as in the more highly purified condition, this starch was used in the raw state. A 2% paste was prepared by mixing the proper amount of dry starch in a little cold water, then adding boiling distilled water, so as to form a uniform suspension, boiling it for 10 minutes and making up to volume with distilled water. The paste is introduced in 10 cc. portions into large test-tubes and these placed in a thermostat kept at 40°; as soon as the temperature is obtained, the proper amount of enzyme is added, in varying quantities, to the tubes, these are well shaken and placed back into the thermostat. As soon as the starch is hydrolyzed, the solution loses its opaque color and becomes clear; this is easily observed by comparing the liquefied and unliquefied tubes. This method can readily be subjected to criticism, since it will give slightly varying results in the hands of different workers, particularly beginners.

To make the end-point clearer, it was decided to add to the starch a coloring substance, which, not interfering with the action of the enzyme, will help recognize the disappearance of the colloidal starch paste. Out of a large number of coloring substances tested, *neutral red* was found to be most suitable. The material is prepared as follows: Place in a large porcelain dish 50 to 100 g. of dry potato starch, pour upon the starch

¹ THIS JOURNAL, 41, 1129 (1919).

100 cc. of 0.5% solution of neutral red, allow the starch to absorb all the color, then wash the colored starch repeatedly with water, till all the supernatant liquid becomes almost perfectly clear. The colored starch is then dried. A 2% paste of this starch is prepared by the method given before. When this colored starch is liquefied by the action of the enzyme, the change from the colloidal to the clear state is readily observed, if no turbid substances were introduced with the enzyme material.

Instead of taking one period of incubation, use is made of the law of the action of diastase upon starch; the product of concentration of the enzyme by the time of action is constant, at least within certain limits of enzyme concentration and time. $E \times T = K$. When the enzyme concentration is too low or too high or the time too short or too long, this law may not hold true. A unit of enzyme is taken as the amount of enzyme which will liquefy 10 cc of 2% "raw" potato starch in 30 minutes at 40°. But, for practical purposes, it is more convenient to use such a concentration of enzyme that would liquefy the starch in not less than one minute and not more than 15 minutes, the tubes liquefied in periods of time outside of these limits should not be considered.

Example.—5 tubes¹ containing 10 cc of the starch solution are placed in the thermostat and kept at 40°. The enzyme solution is diluted 10 times with distilled water (malt flour is extracted for 2 to 4 hours in 20 times the quantity of distilled water). Various quantities of the diluted enzyme are added to the tubes containing the starch solution. The tubes are shaken occasionally so as to insure a thorough mixing. As soon as the starch is liquefied the opaque color of the solution becomes clear (holding the tubes in the light). When the solution in a tube has cleared up, which can be more readily ascertained by comparing with the tubes containing the higher and lower quantities of the enzyme, the time is recorded. One test is given in Table I.

TABLE I.*

Concentration of enzyme in cc ..	0.1	0.2	0.4	0.6	1.0
Liquefaction, minutes.....	12 1/2	6	3	2	Less than 1

Last tube is discarded.

$$K = E \times T.$$

E	T	K
0.1	12.5	= 1.25
0.2	6	= 1.2
0.4	3	= 1.2
0.6	2	= 1.2

$$\text{Av. } K = 1.21$$

* The observations reported in the table are individual determinations.

$$\text{If } T = 30 \text{ minutes, } E = \frac{K}{T} = \frac{1.21}{30} = 0.04.$$

¹ The tubes used in this work were of heavy glass of 100 cc. capacity.

Since the original solution of enzyme was diluted 10 times, we find that the enzyme value of one cc. = $\frac{1}{0.1 \times 0.04} = 250$ units

$$F \frac{30 \text{ min.}}{40^\circ} = \frac{D \times t}{E \times T} = \frac{Dt}{K}$$

F = enzyme value at 40° C. in 30 minutes; D = dilution; t = time of unit standard ($t = 30$ min.); E = quantity of diluted enzyme used; T = time of liquefaction. Thus by taking several tubes and averaging the products we can eliminate certain mistakes that will be made in the reading of the end-point. Given a definite amount of substratum and a definite temperature, the activity of the enzyme can be determined under different conditions of time.

When the stage of hydrolysis corresponding to this end-point, is tested with iodine, it is found to correspond to the point when no heavy blue color is obtained, but only a deep brown to faintly violet-brown color or faint blue-violet color showing that all the starch paste has been transformed into dextrins.

This method is particularly suitable for the study of enzymes that have a starch liquefying power rather large in comparison with the saccharifying power. Kendal and Sherman¹ have shown that, with pancreatic amylase, the hydrolysis of starch tended to come to an equilibrium or to become exceedingly slow when the weight of maltose reached about 85% of the initial weight of starch, even though the amount of enzyme was varied through a fairly wide range. Sherman and Baker² have shown that the ratio of the amylolytic action to the saccharogenic is much higher for *Aspergillus Oryzae* diastase than for malt and pancreatic diastase. The iodine end-point occurred at a much earlier stage in the saccharogenic action, usually when from 20 to 30% of the theoretical yield of maltose had been produced. The *Aspergillus Oryzae* amylase exerts a more pronounced catalytic effect upon the earlier than upon later hydrolysis involved in the transformation of starch through dextrins into maltose. Malt amylase, on the other hand, apparently does not correspondingly catalyze the complete disruption of the material to which the iodine test is due, since the iodine end-point is found only at a much more advanced stage of sugar production with this than with either of the other amylases. The iodine end-point takes place in the case of malt diastase, only when the maltose production has reached from 65 to 95% of the theoretical yield of maltose.

Keeping in mind the fact that the diastase from *Aspergillus Oryzae* produces a good deal of glucose, while malt and pancreatic diastase produce

¹ THIS JOURNAL, 32, 1087 (1910).

² *Ibid.*, 38, 1885, 1638 (1916).

chiefly maltose and only traces of glucose (Sherman and Punett,¹ Davis and Daish²), which will tend to give a still higher "copper value" for the *Aspergillus* diastase, we would expect important differences between the amylolytic and saccharogenic powers of this diastase on the one hand and that of malt and pancreatic diastase on the other hand

The materials used in this study were malt flour (extracted with distilled water for 2 hours), liquid (sirupy) malt extract (Diatophor), and dilute extracts of enzyme from *Aspergillus Oryzae* (commercial name Polyzime) The Lintner values were obtained by the use of a modified Lintner method

TABLE II

Source of enzyme	Lintner value	$F_{40}^{30 \text{ min}}$ Starch liquefying value
Malt flour, No 1	600	120
Malt flour, No 2	600	175
Malt extract	45	100
Polyzime, No 1	180	200
Polyzime, No 2	175	275
Polyzime, No 3	159	250
Polyzime, No 4	170	200

The data brought out in Table II fully confirm the results of Sherman and his associates as to higher amylolytic power in comparison with the saccharogenic power of the *Aspergillus Oryzae* diastase than the malt diastase Comparing the results of the table which was made by one person on the same starch using the same methods, we find that, while the ratio of the liquefying value to the Lintner value of malt preparations was, under the conditions of the experiment, about $1/4$ to $1/5$, that of dilute *Aspergillus Oryzae* enzyme was 1 to 1.5, showing that the latter preparations have about 4 to 6 times as strong a liquefying power for starch in comparison with the saccharogenic power than the malt preparations.

This is in accordance with the investigations of Sherman and Tanberg,³ who have shown that, while in the case of pancreatic amylase the ratio of the amylolytic to the saccharogenic power is 2:1, in the case of *Aspergillus Oryzae* diastase, the ratio of amylolytic to saccharogenic powers is 7:1 to 9:1

Summary.

1. The Lintner method for measuring the saccharogenic action of different enzymes upon starch should not be used for comparative studies of different enzymes, since the end products are not the same in the case of the different enzymes

2. The starch liquefying (iodine) methods with the exception of that

¹ THIS JOURNAL, 38, 1877 (1916)

² *Loc cit*

³ THIS JOURNAL 28 1628 (1916)

of Wohlgemuth, do not give the "liquefaction" of starch by enzymes, but measure the reduction of the starch to substances giving no longer any reaction with iodine, which is arbitrary.

3. In the study of the action of enzymes upon the starches present or embodied in the textiles (process of desizing), the Lintner method and its various modifications are unsuitable, since we are interested not in the sugar production, but in the starch elimination.

4. A method is described for measuring the starch liquefying power (amylolytic action) of enzymes, which is practical and easily manipulated.

5. Comparing the starch liquefying powers of malt enzymes and enzymes obtained from *Aspergillus Oryzae* (water extract used known commercially as Polyzime) the first are found to give a higher Lintner value, while the second give a higher liquefying value. The ratio of the liquefying value to the Lintner value, in the case of the malt preparations, is 1 : 4 to 1 : 5, while in the case of *Aspergillus Oryzae* enzyme it is 1 : 1 to 1.5 : 1, so that the liquefying power of the latter, in comparison to its sugar producing (saccharogenic power), is 4 to 6 times as great as that of the malt preparations.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

ORGANIC CHEMICAL REAGENTS. V.¹ THE PREPARATION OF ALKYL AND ALKYLENE BROMIDES.

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Although alkyl bromides are among the most common of laboratory reagents and although they are prepared by the most elementary reactions met with in organic synthesis their preparation in the laboratory as well as on a relatively large scale requires further improvement. The preparation of ethyl bromide is described in practically all laboratory manuals and yet the methods are so unsatisfactory that two papers² have appeared recently recommending improvements in the process, mainly in an endeavor to avoid the formation of ethyl ether as a by-product. In many reactions in organic chemistry, yields of from 70 to 80% are considered highly satisfactory but not so with the preparation of such simple and extensively used compounds as the alkyl halides. The method described below was found more adaptable to the preparation of alkyl and alkylene bromides than those methods commonly employed; it has been applied to the prep-

¹ For other papers in this series see THIS JOURNAL, 40, 1285, 1930 (1918); 41, 276, 89 (1919).

² J. Chem. Soc., 107, 1489 (1913); 100, 1 (1916)

aration of *n*-butyl bromide, isoamyl bromide, trimethylene bromide, trimethylene chlorobromide, ethyl bromide, allyl bromide, *n*-octyl bromide, and lauryl bromide.

The preparation of alkyl halides from the corresponding alcohols by the use of halogen acids is a very old and well-known process. The use of aqueous solutions of halogen acids, for example the constant boiling mixtures of the halogen acids with water, as developed by Norris and his students,¹ offers distinct advantages over the older procedures. The method is very convenient as a laboratory preparation for student use and for this purpose is without doubt superior to the phosphorus-halide method. In view of the fact that the Norris method is appearing as recommended procedure in laboratory manuals,² this brief note dealing with an essential improvement of the method in its application to primary alcohols should be of value.

Norris has shown that primary, secondary, and tertiary alcohols differ greatly in the ease of reaction with aqueous halogen acids. When a primary alcohol is distilled with one, two, or three moles of aqueous hydrobromic acid (48%), a poor yield of alkyl bromide is usually obtained. Secondary alcohols react with greater ease the result being that satisfactory yields are obtained, whereas tertiary alcohols react even without heating to give almost theoretical results. The shortcoming of the Norris method lies in its application to primary alcohols; although a large excess of hydrobromic acid is used the yields are so unsatisfactory that the method cannot be considered in its present form as of great practical value for the preparation of primary bromides.

In the present work it was observed that the addition of sulfuric acid increased greatly the yields of alkyl bromides obtained by the use of the Norris method. In the tables given below are shown the yields of *n*-butyl bromide obtained when one mole of *n*-butyl alcohol is distilled with various amounts of aqueous hydrobromic acid (sp. gr. 1.49) both with and without the addition of sulfuric acid. Other primary alcohols show a similar behavior but this individual example is chosen because the behavior of *n*-butyl alcohol with aqueous hydrobromic acid in the Norris method has not previously been recorded.

The results in Tables I and II were obtained by placing the materials in a one-liter round-bottom flask and distilling at such a rate that 30 minutes were required for the actual distillation of the alkyl halide. The yields in both series of experiments would be higher if the mixtures were refluxed for a short time preliminary to the distillation.³ In their present form, however, the results are comparable

¹ *Am. Chem. J.*, **38**, 627 (1907); *THIS JOURNAL*, **38**, 1071 (1916).

² *Loc. cit.*, p. 1072.

³ *ibid.*, p. 1072.

TABLE I.

Aqueous HBr used for one mole of <i>n</i> -butyl alcohol moles.	Crude product G	Product after washing with cold conc H ₂ SO ₄ G.	Yield. %
1.....	90	46	34
2.....	105	79	58
3.....	115	89	65
4.....	121	109	80

TABLE II.

H ₂ SO ₄ added to 1.5 moles of aqueous HBr and one mole of <i>n</i> -butyl alcohol moles	Crude product G	Product after washing with cold conc H ₂ SO ₄ G	Yield. %
0.5.....	116	93	68
1.0.....	125	115	84
1.5.....	130	122	89
2.0.....	132	130	94

It is thus seen that the addition of even one mole of sulfuric acid is more than sufficient to compensate for 2.5 moles of hydrobromic acid. This is, however, not the only advantage obtained by the addition of sulfuric acid. When a large excess of hydrobromic acid is used in the Norris method (1 alcohol : 4 HBr), a fair yield of product is obtained (80%), but this product requires washing with sulfuric acid in order to remove unchanged alcohol. When *n*-butyl alcohol is distilled with only 1.5 moles of hydrobromic in the presence of two moles of sulfuric acid, a product is obtained which for the most purposes is sufficiently free from alcohol. From 74 g. of *n*-butyl alcohol there were obtained thus 132 g. of product which after washing with sulfuric acid still weighed 130 g. All of the yields recorded in this paper with the exception of that of allyl bromide refer to material that has been washed with cold conc. sulfuric acid. Other details of manipulation are recorded in the experimental discussion below.

The effectiveness of sulfuric acid as is illustrated in Table II does not depend entirely upon the resulting removal of water from the reaction mixture but is also to be explained by the formation of an alkyl sulfuric acid which probably reacts more readily with hydrobromic acid. The effect of sulfuric acid in preventing the distillation of the alcohol from the reaction mixture is also an important factor. The *n*-butyl bromide prepared by the sulfuric acid method differed in no way from that prepared by the usual Norris method; neither product showed evidences of the presence of unsaturated compounds.¹

The effect of hydrobromic acid upon alcohols in the presence of very large quantities of sulfuric acid has been studied by Niemutowicz² who has suggested this method for the preparation of bromine substitution products of the alkyl bromides. It should be noted that with the con-

¹ *Cl. Ann.*, 379, 291 (1911); 393, 95 (1912).

² *Monatsh.*, 10, 813 (1889).

centration of sulfuric acid used in the experiments recorded in the present work, liberation of bromine by oxidation of hydrobromic acid does not take place.¹

Norris has shown that the reaction between the alcohols and hydrobromic acid becomes slower with increase in molecular weight of the alcohol. Thus 5 g. of normal octyl alcohol heated for one hour with 25.5 g. of hydrobromic acid yielded 3.5 g. of the bromide. When the experiment was repeated using the same quantity of alcohol but decreasing the amount of hydrobromic acid to 15 g. and adding 5 cc. of sulfuric acid, the yield of octyl bromide was 7 g., an improvement of 100%. Similarly, an alcohol with 12 carbon atoms (lauryl alcohol) was found to give a yield of over 90% of the corresponding bromide. The presence of sulfuric acid, therefore, obviates any difficulty found in converting an alcohol of high molecular weight into its bromide. One variation in experimental procedure should, however, be noted. Alkyl bromides of high molecular weight are but slowly volatile with water vapor. In such cases the mixture is heated under a reflux condenser until reaction is complete and the product isolated simply by separation of the layer of insoluble alkyl halide. In this manner there is avoided any decomposition of the product due to heating it with a gradually increasing concentration of sulfuric acid.

The use of sulfuric acid is recommended only for primary alcohol since secondary and tertiary alcohols react readily with aqueous hydrobromic acid alone. Moreover, sulfuric acid has a tendency to dehydrate many secondary and tertiary alcohols. According to the procedure described below, no ether is formed as a by product in the preparation of alkyl halides. A sample of ethyl bromide prepared as above described suffers no appreciable loss in weight when it is washed with conc. sulfuric acid; this is in marked contrast to the results obtained with many of the older methods for the preparation of ethyl bromide.

The favorable results obtained in the preparation of alkyl bromides with aqueous hydrobromic acid to which sulfuric acid has been added will immediately suggest that practically the same result might be accomplished by the use of sodium bromide, water, and sulfuric acid in such ratios as to approximate the proportions used in the above experiments. This prediction is substantiated by experiment, although the yields obtained fall slightly below those obtained with mixtures of constant boiling hydrobromic and sulfuric acids.

For the preparation of alkyl bromides on a relatively large scale the use of hydrobromic acid offers no special disadvantages, since it may be prepared readily by the reduction of bromine by sulfur dioxide in the presence of sufficient water to give the strength of hydrobromic acid desired. The product obtained need not be distilled but may be used directly for

¹ *J. pharm. chim.*, [5] 24, 159 (1891).

the preparation of alkyl halides as has been shown by Bodroux.¹ The fact that $\frac{1}{2}$ mole of sulfuric acid is present for each mole of hydrogen bromide is not a disadvantage since the presence of sulfuric acid is desired and consequently a correspondingly smaller quantity need be added. If constant-boiling hydrobromic acid is desired it may be distilled directly from the sulfuric acid solution, practically no free bromine being liberated. In the preparation of an alkyl bromide it is advisable to use 25% excess of hydrobromic acid; this excess may, however, be recovered by distillation. In the preparation of trimethylene bromide it is found that most of the excess of hydrobromic acid is recovered during the first distillation of the reaction mixture.

In the notes below, two preparations (*n*-butyl bromide and trimethylene bromide) will serve as very satisfactory experiments for student use. Until a few years ago *n*-butyl alcohol and trimethylene glycol were not available as general laboratory reagents because of prohibitive cost but at the present time both of these alcohols are technical by-products and consequently have become suitable materials for laboratory use.

General Method for the Preparation of Alkyl and Alkylene Bromides.

In the experiments given below a general method is employed that will no doubt be applicable to the preparation in yields of 90% and over of many other halogen compounds in addition to the 8 individuals that have been selected. The method consists in treating the alcohol with 25% excess of aqueous hydrobromic acid together with sulfuric acid. The mixture is refluxed in order to convert the alcohol as completely as possible into the corresponding bromide, and the latter is then removed from the reaction mixture by direct distillation. Slight variations from this procedure depend upon the physical and chemical properties of the alcohol used or of the bromide formed in the reaction. For example, in the preparations of ethyl and allyl bromides, the reaction mixture is not refluxed because of the volatility of the former compound, and because of the chemical reactivity of the latter; in the preparation of isomyl bromide a somewhat smaller proportion of sulfuric acid is used in order to prevent charring; while halides of high molecular weight, because of their high boiling points, are separated from the reaction mixture mechanically instead of by distillation.

The Preparation of Hydrobromic Acid.

Hydrobromic acid may be prepared conveniently by the interaction of bromine and sulfur dioxide in the presence of water. Scott² has shown that an exceptionally pure product may be obtained in this manner. The constant boiling mixture of halogen acid prepared by this method

¹ *Compt. rend.*, 286, 206 (1913).

² *J. Chem. Soc.*, 77, 424 (1901).

although distilled from sulfuric acid solution, is free even from traces of bromine. Fortunately in the preparation of alkyl bromides a separation of the hydrobromic from the sulfuric acid is superfluous since the best yields of product are obtained in the presence of sulfuric acid. For certain purposes, however, the constant boiling acid may be required and accordingly the method for its preparation is here described.

In a 3-liter round-bottom flask are placed 1200 g. of bromine, 500 cc. of water, and 1500 g. of cracked ice. A fairly rapid stream of sulfur dioxide from a pressure tank is passed into the flask, the outlet of the gas-tube being placed below the surface of the bromine layer. During the first stage of the reduction the flask should be shaken from time to time in order to avoid the accumulation of sulfur dioxide, or possibly of sulfuryl bromide, which would result in a violent reaction due to the large quantity of material reacting at one time. Although more than 100 reduction experiments were conducted with quantities of bromine varying from $\frac{1}{4}$ to 2 kg., this sudden reaction was noted in only one or two instances in spite of the fact that there was usually no agitation other than that furnished by the entering gas stream.

The flow of sulfur dioxide is adjusted at a rate such that the gas is completely absorbed. One or two hours will serve for the completion of the reaction, at which time the mixture will assume a yellow color which is not removed by further addition of sulfur dioxide. The intensity of color in the reduced solution appears to depend on the quality of bromine used, and with the technical product special care must be taken to observe the exact end-point of the reaction. An excess of sulfur dioxide is to be avoided for the reason given in the section dealing with the preparation of ethyl bromide.

To prevent loss of hydrogen bromide it is advisable to cool the mixture slightly during the progress of the reaction. When the reduction is completed the flask is connected with a condenser and the mixture subjected to distillation. The boiling point of constant boiling hydrobromic acid is $125-126^{\circ}$ at 760 mm. but it must be remembered that in distilling the product from the sulfuric acid mixture the thermometer reading should not be relied upon as an index to the composition of the distillate. Towards the end of the distillation the thermometer will rise to 130° and above, when water with only traces of acid distils from the sulfuric acid residue. Upon redistillation of the product the thermometer reading may be relied upon. For many uses a product free from traces of sulfuric acid is not required and one distillation is sufficient. In such cases the progress of the distillation is followed by specific gravity determinations applied to the distillate. According to the above procedure, 20 kg. of 48% hydrobromic acid were prepared from 10.3 kg. of bromine. The actual time required by one man for the preparation of this quantity was 23 hours.

The Separation of Hydrochloric and Hydrobromic Acids.

In many laboratories alkyl bromides are used in connection with aluminum chloride in the Friedel and Crafts reaction. In such experiments halogen acid may be recovered by absorption in water but this by-product is usually considered valueless because it contains a considerable proportion of hydrochloric acid together with the more valuable hydrobromic acid. Although the boiling point of constant boiling hydrochloric acid (110°) lies close to that of the constant boiling hydrobromic acid (126°), the two products may be separated very readily by means of fractional distillation.

The Preparation of *n*-Butyl Bromide.

(a) **Hydrobromic Sulfuric Acid Method.**--In the preparation of hydrobromic acid for direct use in connection with the manufacture of alkyl bromides, a smaller proportion of water is used than would otherwise be the case. A mixture of 400 g. of bromine and 425 g. of ice is treated in a cooling mixture with sulfur dioxide until the bromine is reduced. 296 g. of *n*-butyl alcohol are then added, and following this there are added in several portions with shaking 200 g. of conc. sulfuric acid. The mixture is heated under a reflux condenser for a period of 2 hours, during which time the formation of butyl bromide is carried practically to completion. The product is accordingly removed from the reaction mixture by direct distillation. The crude material after washing with water weighs 534 g., and a purification with $\frac{1}{2}$ its volume of cold conc. sulfuric acid decreases this quantity by only 4 g. The product is washed with sodium carbonate solution, dried with a small quantity of calcium chloride, and distilled. The yield of product boiling at $101-104^{\circ}$ is 504 g., which corresponds to 92% of the theoretical amount. In a series of experiments in which 3 times the above quantities of materials were used, yields varying from 95% to 97% were obtained consistently. In experiments in which the mixture was distilled directly without refluxing, a yield of only 87% was obtained. The former product is of such purity that washing with conc. sulfuric acid is practically superfluous.

In organic preparations too large a quantity of drying agent is often employed with the resultant loss of a considerable amount of material due to absorption by the drying agent. In the present experiments it was found that after a careful separation of the butyl bromide from the water layer, 15 g. of calcium chloride were sufficient for the drying of 1500 g. of alkyl halide.

(b) **Sodium Bromide Method.**--In a 5-liter round-bottom flask are placed 1350 cc. of water and then with stirring 1545 g. (15 moles) of finely powdered sodium bromide are added. It is advisable to add the salt to water in this manner in place of the reverse procedure in order to avoid

oaking of the sodium bromide. 888 g. (12 moles) of *n*-butyl alcohol are added and finally gradually 2000 g. of conc. (commercial) sulfuric acid. The last half of the acid is added through a dropping funnel after the flask has been connected with a reflux condenser.

The mixture is agitated and finally refluxed during a period of 2 hours. The condenser is then reversed and the alkyl bromide removed by distillation.

The product is purified as in the preceding experiment. The yield is found to be somewhat lower (about 90%), due to the presence of some unchanged alcohol which is, of course, removed by the washing with sulfuric acid. The lower yield is probably due to the decreased solubility of the alcohol in the reaction mixture because of the presence of dissolved salts. On the other hand, when hydrobromic acid is used in place of sodium bromide, the alcohol dissolves completely, and the alkyl bromide separates from the mixture as it is formed. One would therefore predict that with alcohols of still higher molecular weights, still lower yields will be obtained with the sodium bromide method. This prediction was substantiated in experiments with isoamyl alcohol, where the sodium bromide method gave yields of only 70%, whereas the hydrobromic acid method gave yields of almost 90%.

Isoamyl Bromide.

(a) A mixture of 176 g. of isoamyl alcohol (b. p. 128–132°), 480 g. of 48% hydrobromic acid, and 110 cc. of conc. sulfuric acid is placed in an ordinary distilling flask and subjected to slow distillation. The weight of crude product is 277 g. and the weight after purification with conc. sulfuric acid is 240 g., which corresponds to 80% of the theoretical yield. The boiling point of the product is 118–120°. The yield in this preparation can be raised considerably by refluxing the reaction mixture preparatory to the distillation as is shown by the following experiment:

(b) A hydrobromic acid solution is prepared by passing sulfur dioxide into a mixture of 1000 g. of bromine (12.5 moles hydrogen bromide equivalent) and 1100 g. of ice. 880 g. of isoamyl alcohol (10 moles) and 800 g. of sulfuric acid are then added in the order mentioned. The clear homogeneous solution is refluxed gently. Even during the early stages of the heating period the separation of the isoamyl bromide is observed and the reaction appears to be complete after about one hour but it is advisable to continue the heating for one hour longer. The product is isolated as in the preparation of *n*-butyl bromide.

In a typical experiment carried out in accordance with the above directions, a yield of 1435 g. of crude product was obtained. After purification with conc. sulfuric acid this product weighed 1410 g., which corresponds to a yield of 93% before distillation. Upon fractionation it was found, however, that appreciable amounts of high-boiling products were

present and, therefore, the yield of fractionated material boiling over the range 116° to 120° was only 88% to 90%.

Trimethylene Bromide.

A hydrobromic acid solution is prepared from 1275 g. of ice and 1200 g. of bromine by reduction with sulfur dioxide as directed under the preparation of hydrobromic acid. 456 g. (6 moles) of trimethylene glycol and 1200 g. of conc. sulfuric acid are next added in the order given, the sulfuric acid being added slowly.¹ The mixture is refluxed during a period of one hour and then subjected to distillation until no water-insoluble product appears in the distillate. This distillation requires about one hour.

The trimethylene bromide is washed first with 200 g. of cold conc. sulfuric acid, next with a solution containing 50 g. of sodium carbonate, and after the separation from the latter it is dried with 30 g. of calcium chloride. The product is filtered from the drying agent and distilled. In a typical experiment a yield of 1088 g., boiling over the range 162 – 165° , was obtained, which corresponded to 90% of the amount theoretically possible. The lowest yield obtained was 88%, whereas the maximum obtained was 95%.

The yields of trimethylene bromide by the sodium bromide method were somewhat lower. Thus, from 1350 g. of water, 1545 g. of sodium bromide, 456 g. of trimethylene glycol, and 2500 g. of sulfuric acid, a yield of 1110 g. of crude product was obtained, from which, after purification and distillation, a yield of 1030 g. (85%) of bromide was obtained.

Trimethylene Chlorobromide.

A mixture of one mole of trimethylene chlorohydrin and two moles of constant boiling hydrobromic acid is treated gradually with two moles of sulfuric acid. The mixture is refluxed during a period of one hour and then subjected to distillation. The yield of purified product (b. p. 142 – 145°) is 140 g., whereas the theoretical yield is 157 g.

The preparation of ethylene chlorobromide from ethylene chlorohydrin and hydrobromic acid is found to be less satisfactory than the preparation of the trimethylene derivative. The reaction of ethylene with a solution of bromine monochloride in hydrochloric acid² is found to be a more satisfactory method for the preparation of ethylene chlorobromide.

Ethyl Bromide.

In the preparation of hydrobromic acid for the manufacture of ethyl bromide particular care must be taken to avoid the presence of any excess of sulfur dioxide. The evolution of gas during the distillation of the

¹ When dealing with more volatile bromides (ethyl, propyl, and allyl bromides), the sulfuric acid is best added while the flask is attached to a condenser.

² *J. prakt. Chem.*, [2] 26, 380 (1882).

alkyl bromide will invariably result in a large loss of this volatile product (b. p. 38–39°).

To the solution resulting from the reduction of 1000 g. of bromine in the presence of 1075 g. of ice, there are added 500 g. of ordinary 92% alcohol. The flask is attached to a condenser ready for distillation and 1000 g. of conc. sulfuric acid added slowly through a separatory funnel. Because of the volatility of ethyl bromide the mixture is not heated under the reflux but is subjected instead to *slow* distillation. The product after separation from the ice water in which it should be collected is found to weigh 1055 g. A washing with 300 g. of sulfuric acid shows this treatment to be superfluous since a decrease in weight of only 10 g. is observed. This loss is due primarily to loss of ethyl bromide by evaporation.

The product is washed and purified as in the other alkyl bromide preparations. It distils over a range of 38–40° when distilled slowly from a water bath, provided chips of porous plate are added to prevent superheating. Final yields vary from 90% to 95% according to the precautions taken to prevent losses due to evaporation.

In the present experiment, a 25% excess of hydrobromic acid is used. With molecular quantities of materials, the yield will be somewhat lower, usually about 85%, and it is, therefore, questionable whether the method possesses much advantage over that proposed by Weston¹ for the preparation of ethyl bromide.

Allyl Bromide.

To the hydrobromic acid solution obtained by the sulfur dioxide reduction of 480 g. of bromine in the presence of 510 g. of water (added as ice) there are added 385 cc. of aqueous allyl alcohol, which according to bromine titration contain 232 g. of pure allyl alcohol. The flask is fitted to an efficient condenser set for downward distillation and 300 g. of conc. sulfuric acid are added gradually to the warm solution by means of a separatory funnel. The allyl bromide distils from the solution partly during the addition of the sulfuric acid and to facilitate the removal of the halide from the reaction mixture it is advisable to agitate the contents of the distilling flask. This is done best by means of a mechanical stirrer which is introduced through an oil or mercury seal. This distillation requires 1/2 to 1 hour. The crude allyl bromide is washed with dil. sodium carbonate solution, dried over calcium chloride and distilled. The yield of product boiling at 69–72° corresponds to 92–96% of that theoretically possible. A small high-boiling fraction is also obtained and examination has shown this to consist of propylene bromide.

Preparation of Alkyl Bromides of High Molecular Weights.

The method described above is well adapted to the preparation of alkyl bromides of high molecular weights. This was demonstrated by the prep-

¹ J. Chem. Soc., 107, 1489 (1915).

aration of *n*-octyl bromide and lauryl bromide. Since the corresponding alcohols are quite expensive and only small quantities were available, the bromides were prepared only by using 48% hydrobromic acid and sulfuric acid. Because of the slow volatilities of these halides, considerable decomposition is liable to occur during the distillation of the alkyl bromides from the sulfuric acid reaction liquors. It is, therefore, advisable to separate the products from the acid layers by means of a separatory funnel instead of by distillation.

***n*-Octyl Bromide.**—In a 500 cc. round-bottom flask are placed 240 g. of hydrobromic acid (48%), 62 g. of conc. sulfuric acid, and 71 g. of *n*-octyl alcohol. The mixture is boiled under a reflux condenser for 2.5 hours. The solution is diluted with water and the bromide layer separated, washed once with a little cold conc. sulfuric acid, then with water, and finally with dil. sodium carbonate solution. The crude yield is 102 g.; this is dried over a little calcium chloride and distilled. The final yield is 96 g. (91% of the theoretical yield), and the boiling point ranges from 196° to 200°.

Lauryl Bromide.—In a 250 cc. round-bottom flask are placed 70 g. of hydrobromic acid (48%), 22 g. of conc. sulfuric acid, and 40 g. of lauryl alcohol. The mixture is boiled under a reflux condenser for 3 hours and the bromide then isolated as described in the preparation of octyl bromide. The product is distilled under reduced pressure. The yield is 49 g. or 91% of that theoretically possible. The product boils over a range of from 175° to 180° at 45 mm. pressure.

Summary.

1. Aqueous hydrobromic acid obtained by the reduction of bromine with sulfur dioxide in the presence of water is a convenient reagent for the preparation of primary alkyl bromides. The reduction mixture may be utilized directly without a preliminary distillation.
2. Mixtures of constant boiling hydrochloric and hydrobromic acids may readily be separated by means of fractional distillation.
3. A detailed study has been made of the preparation of *n*-butyl bromide from the corresponding alcohol by the hydrobromic acid method; addition of sulfuric acid to the reaction mixture was found to be of more value than an increase in the quantity of hydrobromic acid.
4. A general method is described for the preparation of primary alkyl bromides. The main variations from the Norris-Bodroux Method are (a) the addition of a considerable quantity of conc. sulfuric acid and (b) the recommendation of a refluxing period preliminary to the distillation of the reaction mixture.
5. Detailed directions have been given for the preparations of *n*-butyl bromide, isoamyl bromide, trimethylene bromide, trimethylene chlorobromide, ethyl bromide, allyl bromide, *n*-octyl bromide, and lauryl bromide.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

**ORGANIC CHEMICAL REAGENTS. VI. REAGENTS FROM
n-BUTYL ALCOHOL.**

BY ROGER ADAMS AND C. S. MARVEL

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Until two years ago, *n*-butyl alcohol was a rare organic compound. After the discovery of the method by which starch may be fermented to give acetone and *n*-butyl alcohol, however, this latter substance has become available in large quantities at a low price. It is already in technical use as a solvent but comparatively little advantage has been taken of it for scientific purposes.

In this laboratory, a number of compounds which were needed for certain scientific investigations and which previously had been extremely expensive and difficult to produce, have been easily made from *n*-butyl alcohol. The object of this communication is to point out the new reagents made available in this way and to give detailed methods for the preparation of some of the more desirable ones, such as butyl cyanide, *n*-valeric acid, ethyl *n*-valerate, *n*-amyl amine, *n*-amyl alcohol, *n*-butyl malonic ester, *n*-caproic acid, α -bromo and α -amino *n*-caproic acids.

Butyl bromide can be made from the alcohol in almost quantitative yields and converted with ease into butyl cyanide. This product by reduction gives smoothly *n*-amyl amine; on the other hand by hydrolysis with alkali or by treatment with sulfuric acid and an alcohol, it will give respectively *n*-valeric acid or its esters, compounds which have always been difficult to obtain, particularly in a pure state. By the reduction of ethyl *n*-valerate, *n*-amyl alcohol can be produced in good yields. It is thus possible directly or indirectly to obtain the various *n*-amyl derivatives which have, up to this time, only rarely been used by the organic chemist. Another class of compounds most readily synthesized by means of *n*-butyl alcohol are *n*-caproic acid and its derivatives. Caproic acid is one of the most interesting of the lower fatty acids because of its wide distribution in many fats and oils. Its α -amino derivative known as nor-leucine is especially important on account of its occurrence among the hydrolytic products of brain protein. Pure caproic acid can be very readily prepared by condensing *n*-butyl bromide with malonic ester to give *n*-butyl malonic ester, then saponification and decomposition of this latter compound; the α -bromo caproic acid is best obtained by the bromination of *n*-butyl malonic acid and subsequent loss of carbon dioxide. Since α -amino-*n*-caproic acid or nor-leucine is made directly from the bromo acid, it is thus possible to synthesize this interesting amino acid in quantity.

***n*-Butyl Bromide, Preparation.**—The preparation of this substance

has already been described in detail in a preceding paper on "Alkyl Bromides."¹

***n*-Butyl Cyanide, Preparation.**—In a 5-liter round-bottom flask holding a reflux condenser are placed 690 g. (14 mols) of powdered sodium cyanide, 690 cc. of water, 1575 g. of 95% alcohol and 1575 g. (11.5 mols) of butyl bromide. The mixture is refluxed on a steam bath for 25–30 hours and then cooled. The sodium bromide which has separated, is filtered off by suction and the filtrate distilled with a very efficient fractionating column. The first fraction distilling at 78–85° is chiefly alcohol and can be used again in a subsequent run. The second fraction boiling from 85 to 140° and consisting of a small amount of alcohol, water and butyl cyanide is treated with calcium chloride. Two layers separate, the upper of which is dried over calcium chloride and then distilled. The portion which boils between 138 and 141° is butyl cyanide. The low boiling material if again dried over calcium chloride and redistilled, gives a further quantity of product. The total yield amounts to 720–765 g. (75–80% of the theoretical amount). The success of the whole experiment depends upon the care with which the fractionation is carried out, especially when distilling the first fraction. The complete distillation of such a run as has just been mentioned, using a 20-inch column filled with broken glass should take from 10 to 12 hours. During this process 3 times the amount of liquid should condense and flow back into the flask as distils over. In this way, the alcohol is quite efficiently separated from the other products and the butyl cyanide is then obtained in 80% yields.

Discussion of Reaction.—A few runs were attempted, using 95% alcohol in place of the water and alcohol, but in no case did the yield go above 50% of the theoretical amount.

If efficient fractionation is not carried out, the yield will drop to 60–65% of the theoretical amount. Undoubtedly with a more efficient column than the one mentioned above, the distillation could be carried on more rapidly with just as satisfactory results. In carrying out several runs, using $\frac{1}{2}$ of the quantity described above, yields of 75–80% were also obtained. The 25–30 hours refluxing is quite necessary, since 10 hours' refluxing gives only about 50% yield. A recovery of about 1800 cc. of 80% alcohol is made in each run.

The butyl cyanide always contains a fraction of 1% of isonitrile, which gives it a very objectionable odor. The amount present, however, is comparatively small and for practical purposes may be disregarded.

Butyl cyanide has already been described in the literature² and has been made from butyl bromide and alcoholic potassium cyanide by heating under pressure.

¹ THIS JOURNAL, 42, 299 (1920).

² Ann., 158, 171; 159, 38 (1871).

***n*-Valeric Acid, Preparation.**—In a 3-liter round bottom flask fitted with a reflux condenser are placed 245 g. (5 mols.) of powdered sodium cyanide and 245 cc. of water. After practically all of the sodium cyanide has dissolved, 548 g. of 95% alcohol and 548 g. (4 mols.) of butyl bromide are added. The mixture is refluxed for 30 hours on a steam bath and then allowed to cool. The butyl cyanide, alcohol and excess of butyl bromide are filtered by suction from the sodium bromide which has separated during the reaction. The filtrate is placed again in the 3-liter flask with 216 g. (5 mols.) of sodium hydroxide dissolved in a small amount of water. This mixture is refluxed for about 24 hours on a steam bath and then distilled in order to obtain the alcohol. When most of the alcohol has been recovered in this way, the remainder of the solution is poured into a large evaporating dish and heated over a free flame or over a steam bath for several hours longer in order to be sure that all of the alcohol has been driven off. If this is not done, the final product is invariably mixed with a small amount of ester formed during the acidification process. The sodium valerate solution is now cooled, transferred to a flask and acidified with 300 cc. of about 50% sulfuric acid. This sets free the valeric acid which then is separated, dried over calcium chloride and distilled with a fractionating column. The portion boiling between 183 and 186° is collected and amounts to 330 g. (81% of that theoretically possible). By treating the water layer after acidification with 100 cc. of ether, shaking and separating, then drying over calcium chloride and distilling, a further yield of about 7 g. of material is obtained.

Discussion of Reaction.—If all of the alcohol is not distilled off as described in the above directions, the yield of valeric acid will often drop down to as low as 60 to 65% and as much as 10 to 15% of ethyl valerate will be mixed with the product.

The low boiling fractions of material, by drying a second time with calcium chloride and redistilling, will always yield a small amount more of pure product.

An experiment using 30% sulfuric acid for the hydrolysis of the cyanide was carried out, but even after the refluxing had been carried on for 24 hours, no hydrolysis had taken place.

The early experiments on the preparation of valeric acid were carried out with pure butyl cyanide but the yields were no larger than those obtained by the above procedure. In a 3-liter round-bottom flask with reflux condenser, 230 g. of sodium hydroxide, 520 g. of water, and 250 g. of butyl cyanide are boiled for about 5 hours until the layer of butyl cyanide disappears. To the mixture is now added through the condenser 400 cc. of water, then slowly 300 cc. of 50% sulfuric acid, keeping the mixture cold during the addition. The layer of valeric acid is separated and worked up as already described.

n-Valeric acid has been mentioned many times in the literature. It has previously been produced by the action of alkali on butyl cyanide;¹ by the action of silver on a mixture of ethyl iodide and β -iodopropionic acid;² by the oxidation of α -oxy-*n*-caproic acid;³ by the reduction of levulinic acid with hydriodic acid or by electrolytic reduction;⁴ by the action of hydriodic acid on valero-lactone;⁵ by the action of bacteria on calcium lactate;⁶ by the decomposition of *n*-propyl malonic acid;⁷ by the oxidation of castor oil by nitric acid;⁸ by the action of enzymes on valer-aldehyde;⁹ by biochemical change of α -pyrrolidine carbonic acid;¹⁰ by the action of sodium ethylate on methyl-pyrazolidon.¹¹

Ethyl-*n*-Valerate, Preparation.—In a 5-liter round-bottom flask fitted with a reflux condenser is placed one kg. of 95% alcohol. This is well cooled and one kg. of conc. sulfuric acid is gradually run in. To this mixture is now added 415 g. of butyl cyanide and the whole is refluxed for about 10 hours. After cooling, the reaction mixture is poured into ice water, the upper layer of alcohol and ester separated, dried over calcium chloride and distilled with a fractionating column. The portion boiling at 142–146° is collected. The low boiling fractions, after drying again and redistilling, yield a further amount of pure ester. The total yield of finished product varies between 565 and 595 g. (85–90% of the theoretical amount).

Discussion of Reaction.—Several runs by the method just described were made and in practically every instance very good yields were obtained. An attempt was made to see whether ethyl-*n*-valerate could not be produced from the crude reaction mixture containing butyl cyanide, instead of isolating the pure butyl cyanide. A number of experiments, however, showed that as good results could not be obtained in this way. A very brief description of the procedure is given below because it is possible that this method might be developed into a more satisfactory one. A mixture of 115 g. of powdered sodium cyanide and 115 g. of water with 265 g. of 95% alcohol and 265 g. of butyl bromide was made and refluxed for 30 hours. The layer of butyl cyanide and alcohol was separated from the salt and water, treated with 570 g. of conc. sulfuric acid and the

¹ *Ann.*, 159, 58 (1871); *Ibid.*, 233, 272 (1886).

² *Z. Chem.*, 3, 342 (1869).

³ *Ber.*, 9, 1840 (1876); 10, 231 (1877).

⁴ *Ann.*, 206, 236; 208, 110 (1881); *Z. Electrochem.*, 17, 571 (1911).

⁵ *Ann.*, 226, 346 (1884).

⁶ *Ber.*, 13, 1309 (1880); 14, 1084 (1881).

⁷ *Ibid.*, 17, 2504 (1884).

⁸ *Ibid.*, [2] 23, 438 (1889).

⁹ *Biochem. Z.*, 28, 289 (1910).

¹⁰ *Ibid.*, 37, 490 (1911).

¹¹ *Ann.*, 394, 99 (1912).

mixture refluxed about 10 hours. The product was worked up as described under the preparation using pure butyl cyanide. The yield amounted to about 120 to 125 g. (47-49% of the theoretical amount, based on butyl bromide, or 68-71% based on the butyl cyanide which actually can be obtained from the butyl bromide)

Ethyl-*n*-valerate has already been made by the electrolysis of sodium propionate and potassium ethyl succinate,¹ by the action of alcohol upon *n*-propyl-*n*-butyryl acetic ester;² by the esterification of valeric acid with sulfuric acid and ethyl alcohol.³

n-Amyl Amine, Preparation. —In a 5-liter round bottom flask fitted with a rubber stopper holding a reflux condenser, dropping funnel and efficient mechanical stirrer are placed 276 g. of sodium and 1000 cc. of toluene. The mixture is heated until the toluene commences to boil, at which point the molten sodium is stirred vigorously, a procedure which soon produces an emulsion. A mixture of 166 g. (2 mols.) of butyl cyanide and 300 g. of absolute alcohol is now added to the flask through the dropping funnel (one hour). During this addition and subsequent addition of alcohol and water, the stirring should be vigorous and the temperature regulated so that refluxing is continuous, in general the heat of reaction is all that is required. After all of the butyl cyanide solution has been added, 300 g. more of absolute alcohol is gradually added. To decompose any sodium which may still be present, the reaction mixture is treated slowly with 200 g. of 95% alcohol and then 100 g. of water. About 3.5 hours are required up to this point. The contents of the flask are now steam distilled (3 hours) and the distillate treated with 200 cc. of conc. hydrochloric acid. The toluene is removed and the water, hydrochloric acid, alcohol, amyl amine hydrochloride layer is distilled until most of the alcohol has been removed. As soon as this has been completed, the contents of the flask are poured into an open porcelain dish and evaporated to dryness, the last portion of liquid being removed best on a steam bath. The amyl amine hydrochloride which is obtained is treated with a concentrated solution of 200 g. of sodium hydroxide. The amyl amine separates as a layer, is removed, dried over sodium hydroxide and distilled. The portion boiling at 102-105° is collected as pure material. The low boiling fraction after drying again over sodium hydroxide and redistilling gives an additional amount of amine. From a number of runs, the yields varied between 100 and 120 g. of pure amyl amine (57-68% of that theoretically possible).

Discussion of Reaction.—Although it is quite necessary to have good absolute alcohol, the yield does not drop off so markedly in this experiment

¹ Ber., 28, 2434 (1895).

² Ann. chim. phys., [8] 19, 204 (1910).

³ Ibid., 165, 117 (1873); 233, 273 (1886).

as it does in the reduction of ethyl-*n*-valerate when even the smallest amount of water is present.

In distilling amyl amine, it is advisable to have the side arm of the flask extend a considerable distance into the condenser. This prevents the vapors from coming in contact with the cork and becoming colored.

Stirring should be efficient so as to prevent the caking in the reaction flask when the cyanide-alcohol mixture or subsequent alcohol addition is made.

n-Amyl amine has already been prepared by the action of sodium hypobromite upon *n*-caproic acid amide,¹ by the action of phosphorus pentachloride upon benzoyl-piperidine and then subsequent reduction and hydrolysis.²

***n*-Amyl Alcohol.**—In a 5-liter round-bottom flask, the stopper of which is fitted with a large Y-tube, one branch holding an efficient reflux condenser and the other closed with a stopper, are placed 156 g. of ethyl-*n*-valerate and 2500 cc. of absolute alcohol (d_{25}^{25} 0.785). To this mixture is added through the Y-tube 280 g. of sodium in small pieces at such a speed that vigorous refluxing is continuous. This requires 50 to 60 minutes. The mixture is now refluxed for 2 to 3 hours longer in an oil bath to be certain that all of the sodium has dissolved. The reflux apparatus is replaced by an efficient fractionating column (at least a 20-inch column filled with broken glass) and condenser set downward for distillation. The mixture is distilled from an oil bath; in this way 700 cc. of absolute alcohol is recovered. The residue consisting of amyl alcohol and sodium ethylate is treated with 1000 cc. of water and the distillation carried on again until the temperature of the vapors reaches 83°, indicating that practically all the alcohol is removed. The oil bath must be heated to about 110 or 120° in order to cause the liquid to distil over. In this way between 1800 and 1900 cc. of about 90% alcohol is recovered. The procedure thus far requires 1-1½ days' time. The fractionating column is now removed and the amyl alcohol steam distilled from the reaction mixture, about 500 to 600 cc. of distillate coming over before all the alcohol is removed. This requires about 1.5 hour. The alcohol is separated, dried over potassium carbonate, and distilled. It is quite necessary to dry carefully in order to get a clean product which boils at the right point. By drying again the low fraction from the first distillation a few more grams of good material is always obtained. The yield amounts to 97-105 g. (56-61% of the theoretical amount).

Discussion of Reaction.—The alcohol used for the reduction must be absolute. A lower grade causes the yield to drop very rapidly with a large increase in amount of valeric acid formed.

¹ *Ber.*, 25, 770 (1882); *Ann.*, 233, 253 (1886); *J. Russ. Phys. Chem. Soc.*, 29, 455 (1897).

² *Ber.*, 43, 3596 (1910).

By distilling the 90% alcohol again through a good column and fractionating the residue, 6 or 8 g. more of pure amyl alcohol is obtained. The original distillation must be carried out very carefully and slowly or else a large part of the amyl alcohol comes over with the ethyl alcohol and is consequently lost. Undoubtedly a more efficient fractionating column would give a somewhat better yield and in a shorter period of time.

The alkaline solution after the distillation of the *n*-amyl alcohol may be cooled and acidified. Valeric acid separates, is dried and distilled. The yield amounts to 15-25 g.

The reduction should be run as rapidly as possible in order to prevent the caking of the sodium ethylate which is formed.

n-Amyl alcohol has already been made by several methods, the reduction of valeraldehyde by sodium amalgam;¹ by the hydrolysis of amyl chloride with potassium acetate;² the fermentation of glycerine;³ by the action of silver nitrite upon *n*-amyl amine hydrochloride,⁴ by the action of enzymes upon valeraldehyde,⁵ by the action of silver oxide upon amyl iodide,⁶ by the reduction of acetopropyl alcohol with zinc amalgam and hydrochloric acid.⁷

n-Butyl Malonic Ester, Preparation.—In a 5 liter round-bottom flask fitted with a rubber stopper holding a reflux condenser, separatory funnel, and mechanical stirrer, is placed 2.5 liters of absolute alcohol. To this alcohol is added gradually 115 g. of sodium cut into thin slices. The sodium alcoholate solution is cooled somewhat and 825 g. of malonic ester allowed to flow in slowly through the separatory funnel. Stirring is then started and 685 g. of *n*-butyl bromide is gradually run in. The reaction starts almost immediately and refluxing takes place during the addition of the halide, due to the heat of the reaction. Up to this point, the time required is about one hour. The reaction flask is now placed upon a steam bath and the mixture refluxed until neutral to moist litmus. This point is reached within 2 to 3 hours. The stopper of the flask is removed, a new one holding a condenser set for downward distillation is attached and the alcohol distilled off from a water bath. About half a day is required for this distillation and about 2 liters of alcohol is recovered.

An equal volume of water is added to the residue, the layer of *n*-butyl malonic ester separated and distilled under diminished pressure. A low boiling portion comes over first, consisting of a little alcohol, water and butyl bromide, then a small intermediate fraction of unchanged malonic

¹ *Ann.*, 159, 70 (1871).

² *Ibid.*, 161, 268 (1872).

³ *Bull. soc. chim.*, [2] 48, 803 (1887).

⁴ *Ann.*, 233, 253 (1886).

⁵ *Biochem. Z.*, 28, 289 (1910).

⁶ *Ann. chim. phys.*, [8] 25, 260 (1912).

⁷ *Ber.*, 47, 686 (1914).

ester and finally pure *n*-butyl malonic ester boiling at 144–145° at 40 mm. The yield is 960–990 g. (89–92% of the theoretical amount) of material collected over 5°. Under ordinary pressure the *n*-butyl malonic ester boils at 235–240°.

Discussion of Reaction.—The quality of the alcohol used has a very marked effect on the yield of product. It should be absolute. A trial run with alcohol of 98.4% purity gave a 66% yield.

n-Caproic Acid, Preparation.—In a 5-liter round-bottom flask fitted with a stopper holding a reflux condenser and separatory funnel, 500 g. of potassium hydroxide is dissolved in 500 cc. of water. To this hot solution with frequent shaking, 500 g. of *n*-butyl malonic ester is added slowly through the separatory funnel. The hydrolysis proceeds rapidly and by the time the butyl malonic ester has been added, the saponification is practically complete and the solution is clear. The stopper is removed and the flask heated for 1 or 2 hours on a water bath to drive off most of the alcohol and to insure complete hydrolysis. The stopper, with reflux condenser and separatory funnel, is again attached and the reaction mixture is then acidified with 1500 cc. of conc. hydrochloric acid (sp. gr. 1.19), the acid being added slowly enough to prevent foaming over. This mixture is then refluxed for 4–5 hours, after which time the reaction is nearly complete and a layer of caproic acid appears on the surface. The condenser is set downward for distillation and the solution distilled until practically all of the liquid has come over. From the distillate, the upper layer of caproic acid is separated and 300 to 400 cc. of the water layer is added to the main flask and again distilled off. The caproic acid is again separated and the total aqueous solutions combined and salted out with calcium chloride. About 4 g. of caproic acid per liter of aqueous solution is thus obtained. The distillation as described requires about half a day. The caproic acid is dried over calcium chloride and distilled. It boils at 200–205°. The yield is 200 g. (74% of the theoretical amount).

Discussion of Reaction.—In place of the potassium hydroxide for the saponification of the butyl malonic ester, sodium hydroxide was used in one or two experiments. Under these conditions, the hydrolysis did not proceed nearly so rapidly and it was necessary to boil it under a reflux condenser for 2 to 3 hours to be certain of the completion of the reaction. The difficulty with sodium hydroxide is due to the fact that an organic sodium salt separates, yielding a semi-solid mass, thus making several hours refluxing a necessary procedure to be sure all the ester is saponified. The difference in the price of potassium hydroxide and sodium hydroxide is inconsiderable in comparison with the price of the caproic acid and it is, therefore, advisable to use potassium hydroxide.

After the butyl malonic ester has been saponified to the butyl malonic

acid, several ways of decomposing it to caproic acid besides the method described above were carried out. First, the solution of the potassium salt of the butyl malonic acid was acidified, cooled and extracted twice with ether. This ether solution was dried with calcium chloride and the solvent evaporated. Butyl malonic acid remained behind, which by heating to 160–170°, decomposed rapidly and gave off carbon dioxide. Care had to be taken to condense all the caproic acid which was carried along with the carbon dioxide. Starting with 250 g. of ester, 154 g. (57% of the theoretical amount) of acid thus resulted. Second, the potassium salt of the butyl malonic acid was acidified, refluxed in the way described above and then after cooling, the caproic acid was extracted directly with ether. Under these conditions, some tarry products were always obtained with the caproic acid and the yield of pure material amounted to not over 63% of the theoretical amount. Third, the potassium butyl malonate was made and acidified as in the second procedure just described. Instead of extracting with ether at this point, a steam distillation was carried out until no more caproic acid came over. It required a distillate of 3 to 4 liters before all of the caproic acid was obtained. This distillate was salted out with calcium chloride, the caproic acid separated and dried in the usual way, then distilled. Not over 66% of the theoretical amount resulted. The larger yields of about 75% when the procedure is carried out as in the main experiment, may be due to the longer heating with the acid, during the process of distilling off the caproic acid after it is first formed. At any rate this method, giving the best yields, is at the same time the most convenient one.

If the butyl malonic ester is not heated 1 to 2 hours with alkali, a little acid ester remains undecomposed. This yields upon acidification and decomposition ethyl caproate, a substance which can not be removed easily from the caproic acid by simple distillation.

The methods for the production of caproic acid described in the literature are of two types, that by fermentation and that by synthetic reactions. Thus in the fermentation process for the production of butyric acid, a considerable amount of caproic acid is obtained as a by-product;¹ also good yields of caproic acid result from the fermentation of bran with *mycozyma*.² These methods, however, require a long period of time and particular care in the regulation of the conditions of the reaction. As laboratory procedures they are practically useless. Moreover, there are obtained in these reactions other acids and by-products which are difficult to remove. The synthetic methods described in the literature give in practically every case a clean product, but the cost of the raw material makes these methods almost prohibitive. Thus *n*-amyl cyanide, on hy-

¹ *Z. Chem.*, 1868, p. 522.

² *Ibid.*, 1868, p. 430; 1869, p. 308.

drolysis¹ gives very good results; to produce this cyanide, however, requires starting with *n*-valerianic acid, a substance none too common, converting it first into the aldehyde, then to the alcohol, next to the halide and finally to the cyanide. A second synthetic process has appeared which involves the oxidation of *n*-hexyl alcohol,² but here the same difficulty, namely, the scarcity of hexyl alcohol, presents itself. A more recent method using certain decomposition reactions of piperidine³ is almost as impractical as the preceding ones. Finally, the oxidation of castor oil⁴ with nitric acid yields an appreciable amount of caproic acid. This method, however, gives only a small yield of product and at the same time a mixture of substances from which the pure acid must be fractionated.

α -Bromocaproic Acid, Preparation.—In a 1.5-liter round bottom flask, 216 g. of potassium hydroxide is dissolved in 216 cc. water. To the hot solution 216 g. (1 mol.) of butyl malonic ester is added in portions (10–15 min.), shaking after each addition. The saponification proceeds rapidly. The reaction mixture is then heated for 1.5 hours on a steam bath to complete the reaction and to remove the alcohol which is formed. The flask is set in an ice-salt bath and cooled to 0°, after which the solution is made acid to congo red paper by adding conc. hydrochloric acid (about 500 cc. of acid of sp. gr. 1.19). The butyl malonic acid is now extracted with ether, 3 portions of 200–250 cc. each being used. The ether solution without drying is placed in a flask under a reflux condenser and 50 cc. of bromine (1 mol) is gradually run in (1.5 hr.). The reaction is started at room temperature but the temperature soon rises until the ether boils. The ether solution is now washed with water to remove the hydrobromic acid, dried over calcium chloride and then distilled until all the ether is removed. The crude bromobutyl malonic acid is heated in an oil bath to 125–130° until no more carbon dioxide is given off and the bromocaproic acid thus formed is distilled under diminished pressure. A very small fraction of low boiling material, probably caproic acid, and then the main fraction of α -bromocaproic acid boiling at 148–153° at 30 mm. are obtained. Practically no higher boiling fraction remains. On the first vacuum distillation it often happens that a little carbon dioxide comes off, making it almost impossible to get a constant pressure. Hence, it is advisable to distil all the material over first and then redistil with careful fractionation. The yield of product is 140 g. (71% of the theoretical amount.)

Discussion of Reaction.— α -Bromocaproic acid has thus far been made by the action of bromine on caproic acid in a sealed tube at 140–145°

¹ *Ann.*, 159, 75 (1871).

² *Ibid.*, 163, 199 (1872).

³ *Ber.*, 43, 3599 (1910).

⁴ *Bull. soc. chim.*, [3] 11, 66 (1864).

or by the action of bromine and phosphorus on caproic acid and subsequent hydrolysis of the acid bromide,¹ but neither of these methods is as easy as the one just described.

α -Aminocaproic Acid.—Several experiments were carried out to produce α -aminocaproic acid from α -bromocaproic acid. The exact method of Abderhalden² was used, 140 g. of the bromo acid being employed in each run. The yield of pure product amounted to about 61 g. The first crop of crystals was about 45 g. and the second crop obtained by concentration of the mother liquors to crystallization and addition of an equal volume of alcohol gave 16 g. Further treatment of the mother liquors as described by Abderhalden did not increase the yield appreciably. The material, after washing with alcohol, is practically pure; if small amounts of colored products are present, they are easily removed by crystallization from water.

Discussion of Reaction.—This preparation has already been described in several communications and has been made by the action of ammonia on α -bromocaproic acid,³ the details being given in the paper by Abderhalden.⁴ This investigator claims 100% yields but in the experiments carried out in this laboratory following his directions, only 65% yields of pure product were obtained.

Summary.

1. It has been pointed out that the commercially available *n*-butyl alcohol is a valuable material for the preparation of (A) *n*-amyl derivatives, and (B) *n*-caproic acid and its derivatives.
2. Detailed directions are given for the production of *n*-butyl cyanide, *n*-valeric acid, ethyl *n*-valerate, *n*-amyl amine, *n*-amyl alcohol, *n*-caproic acid, α -bromo-*n*-caproic acid and α amino *n*-caproic acid.

URBANA, ILL.

NEW BOOKS.

Notes on Qualitative Analysis. By LOUIS AGASSIZ TEST AND H. M. McLAUGHLIN. Ginn and Company, 1919. iv + 92 pp. 13.5 x 19.5 cm. Price, \$0.80.

The book contains 24 pages given to the development of the theory of solutions and the law of mass action, followed by directions for experiments on the reactions of the common metallic and non-metallic radicals and tables for use in systematic analysis. A list of 162 questions for students is appended, based upon the practice and theory of qualitative analysis. The periodic table of the elements and a table of atomic weights conclude the volume.

¹ *Z. physiol. Chem.*, 16, 454 (1913).

² *Ibid.*, 86, 454 (1913).

³ *J. prakt. Chem.*, [2] 1, 6 (1870); *Ber.*, 33, 2370 (1900). *Z. physiol. Chem.*, 86, 454 (1913).

⁴ *Z. physiol. Chem.*, 86, 454 (1913).

The authors have prepared the book to be used by their students at Iowa State College, in a one-term course of 6 hours per week, taken before the study of general chemistry has been completed. This calls for an abbreviated treatment of the subject, and the authors are to be highly commended for having kept this limitation honestly in mind in writing their text. The subject matter included is such as can be presented to a class in a term's work and assimilated by them—a qualification possessed by but few texts on qualitative analysis that have been written with that end professedly in view. Those who have searched the market for a suitable laboratory guide for a course of one term know how rare it is to find a "brief" text on qualitative analysis in which the brevity is analytically detectable; and these will thank Messrs. Test and McLaughlin for adding one to the short list of such books.

The experiments on the reactions of the metals are well selected and the methods for systematic analysis are generally simple and workable. The treatment of basic theories in the book is excellent in its scope and stimulating to a beginning class in analysis, but open to much improvement in method and form. There are occasional misstatements and many inaccuracies, all of which should disappear from later editions. There is also improvement possible in the general composition, which suffers from crowding more kinds of material into a paragraph than the best usage permits.

The following statements seem to the reviewer to be errors which the authors will wish to correct in their revision of the work. It is not well to speak of the "direction of a reversible reaction" (p. 9), nor to recommend to students the use of the word "strength" instead of concentration (p. 3), at any rate in a text written from the standpoint of the dissociation theory. In deference to the same theory, the solubility of barium chromate in strong acids should be explained as due to the formation of relatively weak chromic or dichromic acid and not to the formation of the Cr_2O_7 ion (p. 34); and the failure of calcium sulfate solution to produce precipitation in solutions of other calcium salts can hardly be because "the sulfate ions are already in combination with calcium ions." (p. 35). The peculiar behavior of nickel and cobalt sulfides upon treatment with acids is due to their low rate of solution, and not to their insolubility (p. 53). Since hydrogen peroxide does not oxidize chromic hydroxide, it would be better (p. 53) to substitute sodium peroxide for it in the equation, as is actually done in the laboratory directions. These and other statements will need to be doctored somewhat heroically before the authors can be safe from the critical undergraduate who is looking for inconsistencies in his teacher's doctrine.

The book is good enough so that it is to be hoped that the authors will make it better at another trial. It is suggested that a table be inserted

giving the concentrations of reagents used in the work of the course; it would be helpful to students and to teachers who adopt the book for their classes.

ARTHUR E. HILL.

An Introductory Course in Quantitative Analysis, with Explanatory Notes, Stoichiometrical Problems, and Questions By GEORGE MCPHAIL SMITH, Associate Professor of Chemistry in the University of Illinois. The Macmillan Company, New York 1919 x + 206 pp 3 ill. 13 X 19 cm. Price, \$1.75.

This book is divided into 5 parts: Part I, 52 p., dealing with general discussion of the theories and practice of quantitative analytical operations; Part II, 46 p., consisting of typical gravimetric procedures; Part III, 62 p., consisting of typical volumetric procedures; Part IV, 19 p., dealing with methods of solving problems, together with 100 problems for solution by the student, Part V, 15 p., consisting of a series of questions concerning the procedures

In subject matter and in method of treatment the book does not differ greatly from the well-known text by Talbot on the same subject, the chief differences being a much more complete general discussion, a somewhat greater number of experimental procedures (especially in volumetric methods), and the questions concerning the experiments

The general discussion (Part I) is unusually detailed for an introductory manual; much of it is obviously meant to be assimilated gradually by the student as he becomes more familiar with the subject. For the most part the material is well selected and clearly written, although in a few places (e. g., p. 31 and p. 33) description of a process and experimental direction are somewhat confused. The reviewer would suggest that where the subject of "weighing" is to be discussed in such detail (14 p.), a reference to Richards' "The Calibration of a Set of Weights,"¹ and also a specimen table showing the arrangement of data might well be included.

The analytical procedures are very well chosen, and the directions given conform to good analytical practice, being "sufficiently detailed to offer (the student) little opportunity for going astray, and thus to enable him to work successfully without an undue amount of personal supervision." Each procedure is followed by notes designed to explain and emphasize the importance of the different steps. The notes following the electrolytic determination of copper are especially thorough in their treatment.

The reviewer is pleased with the length at which the subject of volumetric analysis is treated, and with the detailed discussion of volumetric technique; he would point out, however, that while most sources of error are minutely treated, there are no directions for the correction of the volume of standard solution for the amount necessary to produce the desired "end-point."

¹ THIS JOURNAL, 22, 144 (1900).

The problems in Part IV serve a useful purpose, and the questions in Part V will be instructive and suggestive to both student and instructor.

Typographical errors are few for a first edition, and the appearance of the book is very satisfactory, although something might be gained at the expense of a few additional pages by placing the separate "Determinations" at the top of the page. There are a few instances of carelessness; thus in the section on "crucibles" only porcelain, quartz, alundum, and platinum are treated, while later "palau (also called rhotanium)" and again "palladium-gold" crucibles are used or referred to without explanation. Also the reviewer takes slight exception to the direction to "fume off the sulfuric acid" (p. 82), but after all these are very minor criticisms.

Altogether, Professor Smith has written a text which will undoubtedly prove a very valuable addition to the present list of texts on Quantitative Analysis, and one which will be found especially suited for use with large classes which are to be given a rather thorough introductory course.

GRAHAM EDGAR.

Recent Discoveries in Inorganic Chemistry. By J. HART-SMITH. Cambridge University Press, Cambridge, England. 1919. 88 pp. 15 X 23 cm. Price, \$1.40.

The author states in his preface that his object has been to give some account of the more important discoveries in inorganic chemistry within the last 15 years, so far as they concern the subject as usually taught in schools. In this he has been successful, for this small volume will certainly furnish a stimulating supply of new material to the teacher of inorganic chemistry, dependent on the somewhat shop-worn information offered by the standard text books on this subject.

The title of the book is, however, unfortunate, unless the adjective "recent" be interpreted from a very philosophical and almost geological point of view. Most of the subject matter is 10 years old, much is 15, and hardly any of it, perhaps naturally enough, is less than 5 years old.

The treatment too is sketchy and incomplete when compared with the similar work by Stewart, or even with the chapters on inorganic chemistry in the annual reports published by the London Chemical Society. In spite of this qualification we have run across many interesting things in this book which we did not know before, and very likely other people will have the same experience.

ARTHUR B. LAMB.

The Chemistry and Manufacture of Hydrogen. First Edition. By P. LYTHERLAND TREN, A.R.S.M. (Mining and Metallurgy), A.I.M.M., Major, R. A. F. Longmans, Green and Co., New York (Edward Arnold, London). 1919. vii + 152 pp. 22 fig. 22.5 X 14 cm. \$3.40 net.

This book was written for English reading as indicated in the preface. It is a general review of what has previously been published and seems to the reviewer to contain nothing new.

The binding is not so good, but the type is clear and the general action

is fair, although it could have been greatly improved if the composition were better balanced by the heavier type for the titled subjects treated. The majority of the figures in the illustrations are old and should have been replaced by later designs.

Chapter I states that hydrogen is used for war purposes, for inflating balloons, in the conversion of olein and other unsaturated fats and their corresponding acids into sterin or stearic acid; and in the production of synthetic ammonia. No mention is made of its use in the cutting and welding of metals or in the production of synthetic stones and other minor uses. Chapter II treats the chemical properties of hydrogen as outlined in chemical text books. However, the omission in this chapter of the properties of hydrogen as a *deodorizing* and purifying agent for fish and vegetable oils is unfortunate. Chapter III relates to the manufacture of hydrogen by chemical methods. The silicon process is treated in this chapter in such detail as to indicate that the author has been in personal touch with the subject. Chapter IV a continuation of the discussion of the manufacture of hydrogen by chemico-physical methods, relates only to the Linde-Frank-Caro process. Chapter V (final) treats of hydrogen production by electrolysis. Four types of electrolyzers (cells) are described, although two of these types are not now manufactured, having been replaced by improved types, the remaining types were in use in the early stages of development of electrolytic cells and now are seldom in demand. This chapter closes with a brief description of the Castner-Keller cell for the production of caustic soda and chlorine, and hydrogen as a by-product. The appendix contains tables and physical constants relating to hydrogen.

Those who desire general information on the subject of hydrogen will find the book interesting reading.

H. L. BARNITZ.

Die Wirkungsweise der Rektifizier- und Destillier-Apparate; mit Hilfe einfacher mathemat. Betrachtungen. By E. HAUSKAND. 25 figs. 3rd Edition. 1916. Julius Springer, Berlin. 14 Mk

This third edition is a complete revision of the earlier editions. It contains all the material of the other editions and takes into account recent work along this line. In the author's words, "Recent work has clarified much that was obscure, and formulas have been derived for the building of distillation apparatus, that for easy derivation and simplicity leave little to be desired." By their application the specifications for apparatus for the separation of two completely miscible liquids by distillation can be determined. The necessary physical data for application to specific substances have been collected from widely distributed sources and this author has added data for a number of liquids which he has determined.

The book is divided into 3 parts. The first deals with the theory of distillation apparatus and describes in detail the characteristics of distilling

apparatus and condensers for periodic and continuous operation. The second part considers the handling and practical application of the apparatus in the separation of a number of mixtures. The number is limited to typical examples and includes ethyl alcohol and water, methyl alcohol and water, acetone and water, acetone and methyl alcohol, acetic acid and water, formic acid and water, ammonia and water and the fractional separation of liquid air. The third part is made up of tables giving data for various mixtures and physical constants for liquids and vapors.

Apparatus for the separation of only two substances is considered as the information on mixtures of more than two liquids is very meagre; and, as the theoretical considerations of all possible combinations would lead to endless complications, the more practical applications have been considered.

R. O. E. DAVIS.

Handbuch der Physikalisch-Chemischen-Technik. By PROF. DR. KURT ARNDT, Privatdozent an der K. Techn. Hochschule zu Berlin. 833 pp. 644 figs. 17 X 24 cm. Ferdinand Enke, Stuttgart 1915. 37 20 Mk.

The author has presented in this book a surprisingly large amount of information on physical-chemical apparatus and technique. The subject matter has been collected from a very large number of scientific journals and publications but particularly from the *Zeitschrift für physikalische Chemie* and *Zeitschrift für Elektrochemie*, references being given to the original articles in all cases.

The scope of the book is, perhaps, best described by referring to the principal points discussed, there being a chapter on each of the following subjects: general laboratory technique, electric ovens, pumps, thermostats, stirring devices, pressure regulation devices, analytical balances, and measurements of length, surface and volume, gas pressure, partial pressure, osmotic pressure, solubility, time, temperature, melting point, boiling point, heat, specific heat, viscosity, surface tension, diffusion, electrical resistance, dielectric constant, transference number, electric current, voltage, and optical constants. Each subject is discussed at some length and well illustrated by figures. Thus in the chapter on measurement of heat quantities, the best forms of apparatus so far developed and the technique for measuring reactions in solutions, the water equivalent of a calorimeter, heats of combustion, heats of evaporation, very small quantities of heat, together with calorimeters for high temperatures are well described and are illustrated by 36 figures.

In the manner of presentation the author has been very successful, an easily readable style having been retained in spite of the great condensation of material that was necessary. The general principles underlying the subject matter of a given chapter are first presented very briefly, yet clearly in a few paragraphs, after which the subtopics are discussed and illustrated. Purely theoretical discussions have been avoided in the book.

as far as was consistent with the proper presentation of the subjects. The book contains a very detailed table of contents as well as an author and subject index.

This manual should prove to be especially useful to the less experienced investigators in physical chemistry, for in no other book is the field so thoroughly covered and so well illustrated. It should also be of assistance to those already familiar with the field, by furnishing valuable suggestions in the matter of technique and apparatus to meet special requirements.

JOSEPH M. BRAHAM.

Die Katalyse. Die Rolle der Katalyse in der Analytischen Chemie. By DR. GERTRUD WOKER, Privatdoz. University of Bern. Vol II, Part I, Inorganic Catalysts. 25 X 16¹/₂ cm. 803 pp. 13 illustrations. Ferdinand Enke, Stuttgart. 1915. 28 Mk.

Many will recall the first volume of this work by Dr. Woker, dealing with the general principles of catalysis as applied in particular to analytical chemistry, which appeared in 1910 as Volumes 11 and 12 of the excellent series of monographs entitled, "Die Chemische Analyse," edited by Margosches. While that volume was bewildering in its effect upon the reader, nevertheless, it presented in collected form a great amount of material dealing with the theory of catalysis, and displayed an amazing amount of erudition on the part of its author.

The present volume, (Nos. 21 and 22 of the same series) with its nearly 800 pages of text and its innumerable footnotes and references, surpasses even the first volume in the profuseness and completeness of the assembled material. The subject matter has been arranged under the heads of the various catalysts involved; thus, the chapters are entitled, "Catalysis by Water; Hydroxyl Ion, Hydrogen Ion, Iodide Ion, Neutral Salts; Heavy Metals; Oxides and Salts; Gases and Vapors; Light, and Agents of Unknown Origin."

The authoress points out in her introduction that in this field we must still heed the warning of von Lippmann, uttered long ago, that, "Catalysis today is revered almost as a fetish; that people seem to consider phenomena as adequately explained merely by calling them *catalytic*, when really all that has been done is to substitute for the unknown quantity x another equally unknown quantity y . As Berzelius, the discoverer of catalysis said in 1836 to Wohler: 'God forbid that we trust too much to catalytic force'." But to anyone who reads these volumes by Miss Woker, there can be no question of the fertility of the idea of catalysis, nor of the light which a study of this phenomenon and of reaction velocity has and still can shed upon the field of chemical analysis and of inorganic chemistry.

The publishers promise a second part of Volume II nearly as large as the first, to be devoted to biological chemistry (The Ferments).

ARTHUR B. LAMB.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Iro Ramsen)

TWENTY-SIXTH ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS.

DETERMINATIONS PUBLISHED DURING 1918 AND 1919.

BY GREGORY PAUL BAXTER.

Received February 12, 1920

For the first time since 1916 the International Committee on Atomic Weights¹ recommends changes in its table. In the case of elements affected by the report the old and new values are given below:

	1916.	1920.
Argon.....	39.88	39.9
Boron.....	11.0	10.9
Columbium.....	93.5	93.1
Gallium.....	69.9	70.1
Nitrogen.....	14.01	14.008
Thorium.....	232.4	232.15
Yttrium	88.7	89.33

The individual determinations published during the last two years are as follows:

Helium.—Guye² continues his discussion of general errors affecting atomic weight determinations, with especial reference to exact weighing and the microbalance. Taylor's³ results on the density of helium are recalculated, with the result 3.998 for the atomic weight of this element.

¹ THIS JOURNAL, 41, 1881 (1919).

² *J. chim. phys.*, 16, 46 (1918).

³ *Phys. Rev.*, 10, 611 (1917).

Boron and Fluorine.—Smith and van Haagen¹ converted weighed quantities of very carefully dehydrated borax into a number of different sodium salts, by evaporation in a platinum flask with methyl alcohol and acid. In some cases the acid used during the expulsion of the methyl borate corresponded to the sodium salt finally weighed. In others formic acid was employed in the preliminary evaporation and the formic acid was eventually displaced by the acid finally combined with the sodium. In 3 experiments the sodium fluoride which was first obtained was weighed and then was converted to sulfate quantitatively, and in one experiment a similar process was adopted with sodium chloride. Except in the case of sodium fluoride and sulfate, one experiment only of each sort was completed. The same specimen of borax was used throughout. This was prepared by combining sodium carbonate with a slight excess of boric acid, and crystallizing the product many times with one intermediate fusion. Vacuum weights are given. C = 12.005; N = 14.010; Na = 22.997, S = 32.069, Cl = 35.457.

Expt	Wt of Na ₂ B ₄ O ₇	Wt of salt	At wt B	At wt F
		NaCl		
IV	0.89853	0.52112	10.896	19.002
		Na ₂ SO ₄		
		0.63313	10.905	
		NaF		
V	0.69695	0.29042		19.005
		Na ₂ SO ₄		
		0.49113	10.901	19.006
		Na ₂ SO ₄		
VI	1.59374	1.12315	10.898	
		NaNO ₂		
VII	1.86458	1.57250	10.900	
		Na ₂ CO ₃		
VIII	1.97702	1.03946	10.903	
		NaF		
IX	1.99197	0.83003		19.004
		NaF		
X	1.60201	0.66757		19.006
		Na ₂ SO ₄		
		1.1889	10.902	19.008
		NaF		
IX	2.64768	1.10329		19.005
		Na ₂ SO ₄		
		1.86597	10.896	19.002
		Average,	10.900	19.005

The International Committee on Atomic Weights has adopted this new value for boron.

Carbon.—Stahrioss² has determined the densities of acetylene, ethylene

¹ Carnegie Inst. Publication, 267, 1918

² J. chem. phys., 16, 175 (1918)

and ethane. Acetylene was prepared by dropping a mixture of calcium carbide, potassium dichromate and ferrous chloride into water, and, after scrubbing and drying, was fractionally distilled. The numbers represent the weight of the liter in grams. In the last column the correction for deviation from Boyle's law is applied.

Globe A 349.58 cc.	Globe B 578.40 cc	Globe C 893.10 cc	Average	Corrected average
1 17876	1 17905	1 17871	1 17884	1.17926
1 17849	1 17897	1 17921	1 17889	1 17925
1 17842		1 17841	1 17842	1 17879
Average,				1.17910

Ethylene was prepared from ethyl alcohol and phosphoric acid, and also, after purification and drying, was purified by fractional distillation.

Globe A	Globe B	Globe C	Average	Corrected average
1 26030	1 26031	1 25997	1 26019	1 26094
1 26177	1 26078	1 26183	1 26146	1 26210
1 26031	1 26001	(1 26396)	1 26016	1.26096
Average,				1.26133

Stahrioss prefers to reject the second series. If this is done the average is 1 26095.

One sample of ethane was made by allowing ethyl bromide to act upon magnesium and decomposing the product with water. The gas was purified and fractionated

Globe A	Globe B	Globe C	Average	Corrected average
1 35466	1 35430	1 35502	1 35466	1.35632
1 35400	1 35482		1.35411	1.35621
	1 35416	1 35521	1 35468	1.35668
	1 35399	1 35381	1 35390	1.35585
Average,				1 35679

A second sample of ethane, resulting from the action of ethyl cyanide upon sodium, was purified as above.

Globe A	Globe B	Globe C	Average.	Corrected average.
1 35493	1 35459	1 35525	1 35492	1 35684
1 35450	1 35456	1 35525	1 35477	1 35701
1 35450	1 35440	1 35489	1 35460	1 35687
Average,				1 35690
Average of both series,				1.35660

If the results of the last 7 experiments are averaged with 12 previously obtained by Baume and Perrot¹ and corrected, the final value 1.3565 is obtained.

It is stated that by the method of critical constants the atomic weight of carbon is calculated to be 12.00, but details of the treatment of results are lacking.

¹ *J. chim. phys.*, 7, 369 (1909)

Batuecas¹ also has determined the density of ethylene, prepared by the reaction of alcohol on (1) phosphoric acid, (2) boric acid, (3) sulfuric acid, and (4) by the catalytic decomposition of alcohol. After purification and drying the ethylene was fractionally distilled. In the following table the correction for deviation from Boyle's law has been applied:

Method of preparation.	Globe RT 615 23	Globe 3 795 61	Globe 4 795 70	Average
1 preliminary	1 25985	1 26033		1.26009
1	1 26047	1 25999	1 26041	1 26029
1	1 26002	1 26022	1 26052	1.26025
2		1 2604		1 26045
3	1 26029	1 26003	1 26031	1.26021
3	1 26047	1 26050	1 26052	1.26050
4	1 26012	1 26037	1 26047	1 26032
4	1 26029	1 26046	1 26031	1 26035
		- -		
Average,	1 26022	1 26029	1 26042	1 26031

By comparison with oxygen the molecular weight of ethylene and the atomic weight of carbon ($H = 1.0077$) are computed

By the molecular volume method	$C = 11.996$
By the limiting density method	$C = 11.999$
By the critical constant method	$C = 12.005$

Argon.—Leduc² finds the specific gravity of argon referred to air at 0° to be 1.3787, and the coefficient of deviation from Boyle's law at 14° to be 10.2×10^{-6} per cm. of mercury between one and five atmospheres. The molecular and atomic weight of argon by the method of limiting densities is found to be 39.91. The International Committee has adopted the value 39.9.

Gallium.—Richards, Craig and Sameshima³ purified gallium trichloride by 3 distillations in chlorine at $220-230^\circ$, 3 in chlorine at 175° , 3 in nitro-gen at $90-110^\circ$ and 5 at $65-80^\circ$ in vacuum. In one preliminary experiment 0.43947 g. of the chloride was weighed in an exhausted glass bulb, and, after solution was compared with silver. The chloride required 0.80587 g. of silver and yielded 1.07087 g. of silver chloride, all in vacuum. These data give the values 70.09 and 70.11 for the atomic weight of gallium. The value 70.1 has been provisionally adopted by the International Committee on Atomic Weights.

Bromine.—Guye⁴ discusses the calculation of the deviation of a gas from Avogadro's rule by the method of compressibilities, with special reference to hydrobromic acid, and from the data of Moles⁵ and Reiman⁶

¹ *J. chim. phys.*, 16, 322 (1918)

² *Compt. rend.*, 167, 70 (1918); *Ann. Phys.*, 9, 5 (1918)

³ *THIS JOURNAL*, 41, 131 (1919)

⁴ *J. chim. phys.*, 17, 141 (1919)

⁵ *Ibid.*, 14, 389 (1916).

⁶ *Ibid.*, 15, 293 (1917).

finds the value of $1 + \lambda$ at one atmosphere to be 1.00934. On the basis of this value Guye¹ computes the atomic weight of bromine to be 79.920, using the average corrected weight of the normal liter as found by Moles and Reiman, 3.64423, and that of oxygen, 1.42904 ($1 + \lambda = 1.00097$). If the individual values of λ of Moles, 3.64441, and Reiman, 3.64404, are used, however, the values 79.924 and 79.915 are obtained for bromine.

Yttrium.—Kremers and Hopkins² have determined the ratio of yttrium chloride to silver, using yttrium salt which had been purified for a previous investigation.³ Vacuum weights are given. $\text{Ag} = 107.88$; $\text{Cl} = 35.46$.

Sample.	Wt. of YCl_3	Wt. of Ag.	Ratio YCl_3 3 Ag	At. wt. Y.
O_1 -s.....	3.31143	5.47636	0.60468	89.32
O_2 -s.....	2.31979	3.83587	0.60476	89.34
O_3 -s....	2.26815	3.75045	0.60477	89.35
O_4 -s....	2.29376	3.79302	0.60473	89.33
T_{11}	2.00731	3.31977	0.60465	89.31
R_4	1.97610	3.26827	0.60463	89.30
R_4	2.17949	3.60389	0.60476	89.34
Average,				89.33

This value has been adopted by the International Committee on Atomic Weights.

Tin.—Brauner and Krepelka⁴ have compared tin tetrabromide, distilled in vacuum, with silver.

Wt. of Salts	Wt. of Ag	Ratio, SnBr_4 4 Ag	At. wt. Sn.
<i>Preliminary Series.</i>			
1.11964	1.10206	1.01595	118.73
1.97428	1.94354	1.01579	118.67
2.35469	2.31788	1.01588	118.71
Average,			118.70
<i>Final Series.</i>			
5.11788	5.03796	1.01586	118.702
2.46873	2.43035	1.01580	118.674
0.99510	0.97961	1.01581	118.679
1.69834	1.67172	1.01592	118.727
3.54265	3.48737	1.01585	118.697
3.82180	3.76199	1.01590	118.717
Average,			118.699

This value is in close agreement with the recent results of Briscoe, and Baxter and Starkweather.

Dysprosium.—Kremers, Hopkins and Engle⁵ purified dysprosium material by fractionation of the (1) bromate and (2) ethyl sulfate. Then

¹ *J. chim. phys.*, 17, 171 (1919).

² *THIS JOURNAL*, 41, 718 (1919).

³ *Ibid.*, 38, 2332 (1916).

⁴ *Rozprawy Chém. Akademii iłd. a. uniw.* The data have been communicated privately to Dr. Krepelka.

⁵ *THIS JOURNAL*, 40, 598 (1918).

weighed quantities of oxide were converted to chloride in a weighed quartz flask. As the oxide was subsequently found to contain carbonate, the results of this series of experiments are rejected by the authors, and therefore are not given here. Next, the chloride, which had been rendered anhydrous by fusion in a current of hydrogen chloride, was compared with silver in the usual way. Weights are corrected to vacuum. $\text{Ag} = 107.880$.

Sample	Wt. of D_2Cl_2	Wt. of Ag	Ratio $\frac{\text{Ag}}{\text{D}_2\text{Cl}_2}$	At. wt. Dy
Ethyl sulfate	1 04079	1 26301	1 20309	162.62
	1 95604	2 35181	1 20334	162.57
	1 47475	1 77504	1 20362	162.51
	1 26253	1 51991	1 20386	162.45
	0 90677	1 20033	1 20421	162.38
	2 25129	2 70902	1 20471	162.49
	2 23374	2 68506	1 20438	162.56
Bromate	1 20763	1 45125	1 20430	162.56
Average,				162.52

Erbium.—Wichers, Hopkins and Balke¹ made a comparative study of methods for the separation of yttrium from erbium and completed preliminary experiments in which a weighed quantity of erbium oxide was converted to chloride, which was weighed. The subsequent discovery that erbium oxide made from oxalate contains carbonate even after ignition at 900° , not only makes the results of these experiments of doubtful value, but also, as the authors point out, throws suspicion on all experiments where the weight of a rare earth oxide made by ignition of the oxalate has entered into the computation of the atomic weight.

Radioactive Lead.—Hönigschmid² found the atomic weight of thorium-lead used by Soddy in density determinations to be 207.77.

In another investigation upon thorium-lead, Hönigschmid³ has determined the atomic weight of lead from 3 specimens of Ceylon thorianite, of the following composition

	I	II	III
Thoria and rare earths	78.2	79.11	72.52
Uranium oxide	11.9	12.2	18.1
Pb.	2.34	3.11	3.5
At. wt. Pb.	207.21	206.91	206.84

Fayans, Richter, and Rauchenberger⁴ separated the lead from thorite containing 30.1% of thorium, only 0.44% of uranium, and 0.35% of lead. Three determinations of the atomic weight of the lead by Hönigschmid gave an average value of 207.90.

¹ THIS JOURNAL, 40, 1615 (1914).

² *Fysisk Z.*, 18, 114 (1917).

³ *Ibid.*, 19, 436 (1918); *Z. Elektrochem.*, 25, 91 (1919).

⁴ *Sitzb. Heidelberger Akad. Wiss.*, 1918, p. 28, *J. Chem. Soc.*, 116, II, 7.

Davis¹ purified ordinary lead and lead from samarskite by crystallization of the nitrate and chloride. Analysis of the chloride gave the value 207.27 for the atomic weight of common lead and 206.30 for that of radioactive lead.

The samarskite was found to contain 12.21% uranium and 1.03% thorium.

J. J. van Laar² applies a method of critical constants to the determination of the atomic weights of several elements, using the density data of various experimenters, with the following results: H = 1.00770; He = 4.000; C = 12.001; N = 14.004; S = 32.060; Cl = 35.460; Br = 79.922.

Moles³ discusses critically revisions of atomic weights published in 1917.

Guye and Renard⁴ consider the distribution of errors in determinations of atomic weights.

Guichard⁵ briefly compares methods of atomic weight investigation.

CAMBRIDGE, MASS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

A SIMPLE, RAPID METHOD FOR THE DETERMINATION OF HALOGEN IN ORGANIC SUBSTANCES.⁶

BY W. A. VAN WINKLE AND G. MCP SMITH

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Introduction.—The present investigation is a continuation of work taken up by G. McP. Smith at the request of the Bureau of Mines shortly after our entry into the war, which led to a scheme for the rapid, approximate determination of certain gases (e. g., of chloropicrin) in the air by a method of simple combustion.

In view of the difficulties involved in many of the available methods for the determination of halogen in organic compounds, this method of simple combustion was considered worthy of further investigation. And it will be shown in the experimental part that the method in its simplest form is capable of wide application, and that it can be depended upon to furnish reliable values.

Previous Work.—This method of analysis has frequently been proposed, and nothing could be simpler in principle. Trouble has always been met with, however, in carrying out the combustion, and often in

¹ *J. Phys. Chem.*, **22**, 631 (1918).

² *J. chim. phys.*, **17**, 266 (1919), *Chem. Weekblad*, **16**, 1243 (1919).

³ *J. chim. phys.*, **16**, 350 (1918).

⁴ *Arch. sci. phys. nat.*, **44**, 402 (1918).

⁵ *Bull. soc. chim.*, **21**, 238 (1917).

⁶ Excerpt from a thesis submitted to the Graduate Faculty of the University of Illinois by W. A. Van Winkle, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

determining halogen in the combustion products. Some of the procedures require a combustion tube to be packed with substances which may fuse upon the glass, and many require close attention throughout the combustion.

Warren¹ burns the substance in a stream of oxygen, absorbing the halogen with various oxides, as zinc oxide, lead dioxide and cupric oxide, placed forward in the tube. The halogen is extracted from the oxide with sodium carbonate solution, and is determined in the extract. Only chlorine compounds were studied, and the results leave much to be desired.

Brügelmann² also burns the substance in oxygen, but uses calcium oxide to absorb the halogen; otherwise his procedure is much the same, except that he titrates according to Volhard, and obtains values better than Warren's.

Dennstedt³ recommends burning in oxygen, with platinum black as a catalytic agent, and absorbing the halogen with lead dioxide in the case of chlorine or bromine compounds, and with metallic silver in the case of iodine compounds. With lead dioxide, he follows Warren's subsequent procedure; with silver, the increase in weight is ascribed to iodine.

Plimpton and Graves⁴ introduce the vaporized organic halogen compound into the flame of a specially constructed Bunsen burner, when the halogens are obtained in combination with hydrogen, and also in the free state. The products are absorbed in sodium hydroxide solution, and after reduction the halogen is precipitated with silver nitrate. Apparently it is not easy to control the combustion, which must be given constant attention. Good values are given for about 10 compounds.

Zulkowsky and Lepéz⁵ burn the organic substance in a stream of oxygen with platinized quartz as a catalyst. In the case of chlorine compounds, they use ammoniacal hydrogen peroxide as the absorbing agent, and in that of bromine or iodine compounds a solution of potassium iodide. With the latter solution, the determination is iodometric. Chlorine compounds present difficulties, since the platinum tends to retain chlorine, which is wholly removed only with excessive heating. Their method is complicated, but they find good values in most of the analyses, which check well with figures obtained by the Carius method.

Klason⁶ suggests burning the substance in a stream of air or oxygen mixed with nitrous fumes, the latter being introduced ahead of the sample, and the burning taking place in the presence of platinum foil. In

¹ *Z. anal. Chem.*, 5, 174 (1866).

² *Ibid.*, 15, 1 (1876), 16, 1 (1877).

³ *Ber.*, 30, 1590 (1899).

⁴ *J. Chem. Soc.*, 43, 119 (1883).

⁵ *Monatsh.*, 5, 537 (1884).

⁶ *Ber.*, 19, 1910 (1886).

the case of bromine or chlorine compounds, he recommends passing the products into silver nitrate solution; with iodine compounds, into water, the iodine being taken into solution with sulfurous acid, the liquid neutralized, and the iodine precipitated with silver nitrate. No analytical data are given.

Reid¹ burns the sample in a boat using a slight excess of oxygen, and absorbs the products near the exit of the combustion tube, at about 270°, with finely divided silver and silver oxide, contained in a small silver boat. After the combustion Reid reduces the residual silver oxide at a temperature of about 170° by means of a current of hydrogen. Having the weight of the silver boat plus the finely divided silver, of the boat and silver plus the silver oxide, and of the boat and its contents after absorption and reduction, "To find the weight of the halogen absorbed, deduct from the weight of the silver boat containing the oxide, the amount that this oxide would lose on reduction, and subtract this corrected weight from the final weight of the boat." The method, though complicated and requiring experience and care, appears to be capable of yielding good results.

Experimental.

Outline of Method.—The sample, carried by means of a current of air, is drawn through a strongly heated quartz tube, and the combustion products are passed into a suitable absorption vessel containing sodium hydroxide solution. Any oxyhalogen salts are then reduced and the halogen estimated by the Volhard method.

Development of a Suitable Furnace and Combustion Tube.—In the first experiments a 22 mm. quartz tube was heated in a 30 cm. Hoskins electric combustion furnace; but, owing to the time consumed in sweeping out the gaseous products, this tube was early replaced by one 6–7 mm. in diameter, and this size was adopted in the final apparatus. To allow a better control of the combustion process, a longer furnace containing 3 separate 25 cm. heating units was designed and built. This furnace could be heated in sections, as desired, the middle unit being so constructed as to permit of its use either as a 12.5 cm. or as a 25 cm. unit. In this way, 12.5, 25, 38, 50 and 75 cm. lengths of the furnace could be brought into action.

In over 100 determinations made with these furnaces, mostly with chloroform,² it was found that if the ratio of air to volatile material was not

¹ THIS JOURNAL, 34, 1033 (1912).

² The lowest satisfactory combustion temperature in the case of chloroform, with the use of air, appears to be about 900°. For example, with a sample containing 88.4% of chlorine (mean of 7 Carius determinations), the following results were obtained (30 cm. furnace): 900°, 88.60%; 850°, 88.45%; 800°, 84.97%; 750°, 78.90%. At about 600°, particularly with a slow current of air, an appreciable deposit of fine needle-like crystals settled in the cool portion of the tube. Recrystallized from alcohol.

allowed to change suddenly in favor of the latter, due to excessive heating of the sample holder, the combustion could be depended upon to go smoothly, and without much attention. It was found advisable to place a thermometer beside the sample holder, and to warm both gradually (in a bath) to a temperature 10 to 30° below the boiling point of the sample.

A few runs made with tank oxygen showed no improvement over air.

Although it was possible to obtain good results with chloroform and carbon tetrachloride, with the use of these furnaces, the first bromine compound studied, ethyl bromide, revealed a serious defect in the apparatus. Heavy bromine vapors condensed in the projecting end of the tube, and could not be completely removed without undue trouble and loss of time. At this point it was found that the operation could be materially simplified, and much time saved, by means of the gas-heated tubes to be described later (see Fig. 1). Combustion furnaces of the ordinary, slow-cooling, type were therefore discarded.

Sample Holders and Absorption Tubes.—Many types of sample holder were tried, several with success, but the most reliable are those shown in Figs. 1 and 2. And, while several types of absorption apparatus gave good results, the type finally adopted is considered decidedly superior for this work. It is illustrated in Fig. 1.

Reduction of Oxy-halogen Salts, Precipitation, and Titration.—Before precipitating the halogen in the absorption liquid, it is of course necessary to reduce the oxy-halogen salts which are present. For this purpose, hydrogen peroxide, metallic zinc, and sodium sulfite were studied.

Using a known weight of carefully purified potassium chlorate as a standard, and reducing with sodium sulfite, each of 8 gravimetric determinations yielded the theoretical weight of silver chloride. This reagent was therefore adopted. But before the addition of silver nitrate it is, of course, necessary to remove the excess of the sulfite. This was originally accomplished by boiling the slightly acidified solution; but so much time was consumed in this operation that oxidation by means of potassium permanganate was substituted. Test analyses showed the two methods to be about equally accurate.¹

The procedure finally adopted is as follows. The absorption solution was made up in each instance by mixing 25 cc. of approximately 5 *N* sodium hydroxide solution and 10 cc. of 2 *N* sodium sulfite solution. If these melted at 229° corr, and gave a copious test for chlorine; hexachlorobenzene was indicated.

As to the length of furnace heated, studies made at about 900° show that low values are likely if this is less than about 20 to 25 cm. Since the extremities of an electric combustion furnace fall off decidedly in temperature, this means the use of 30 to 38 cm. heating coils.

¹ Using pure NaCl, KBr, and KI as standards, adding Na₂SO₄, acidifying with dil. H₂SO₄, and comparing the two methods, the following values were found by the

these reagents were not halogen-free, the quantities used were accurately measured by means of pipets, since, in that case a correction had to be made in accordance with the results of duplicate blanks run with the absorption solution alone.¹

After absorption, the solution was treated with 25 cc. of dil. sulfuric acid, and the excess of sulfite oxidized with permanganate solution, added to the appearance of a faint pink color. Standard silver nitrate solution was then added, about 5 cc. in excess, followed by a few cubic centimeters of dil. nitric acid; if, on shaking for a few moments, the precipitate did not coagulate, the suspension was warmed on the steam bath. The precipitate was filtered in the cold with suction and washed with 1% nitric acid, even in bromine and iodine determinations, since the sodium hydroxide and sulfite of commerce contain traces of chloride. Finally, 5 cc. of ferric alum indicator was added to the filtrate, followed by enough dil. nitric acid to lighten the color, and the solution was then titrated with standard thiocyanate solution, of half the normality of the silver solution used.²

For the sake of uniformity, all titrations were carried out in artificial light, and for this purpose a special titration table was designed and constructed. With the burets mounted upon this table, the titration was performed in the light from two 100-watt, nitrogen-filled, blue glass (or daylight) lamps, one behind each buret, in a compartment lined with asbestos board, but faced with ground glass. The base beneath the burets was of glass, with its under side covered with white (lithopone) paint. A special lamp was provided to facilitate reading the burets.

Check Analyses.—Owing to the difficulty of always obtaining pure organic compounds, it was decided to check the combustion results by some standard method of analysis, and for this purpose the Carius method was selected, in spite of its drawbacks, as being the most reliable.

Volhard method. (The NaCl to which no sulfite was added was analyzed gravimetrically. This salt was used in standardizing the silver nitrate solutions employed throughout the work.)

	Sulfite boiled off	Sulfite oxidized	No sulfite added
NaCl	60 45-60.66% Cl (8 determinations)	60 42-60 71% Cl (5 determinations)	60 63 and 60.65% Cl (gravimetric)
KBr	67.58 and 67.59% Br	67.71 and 67.68% Br	67.55 and 67.54% Br
KI	76.66% I	76.69 and 76.63% I	76.51 and 76.55% I.

¹ By preparing these reagents in quantity, it is unnecessary to make repeated blank runs. In this investigation halogen-free reagents were used at the start, but it was later found more convenient and just as accurate to use the ordinary stick sodium hydroxide and the sodium sulfite of commerce.

² The dil. H₂SO₄ and HNO₃ are made by mixing one vol. of conc. acid with 3 vols. of water. The KMnO₄ solution used to oxidize the sulfite is a saturated solution of the salt. The indicator is made by adding conc. HNO₃ to a saturated solution of ferric alum, to the complete lightening of the deep brown color. The standard solutions recommended are 0.1 *N* and 0.2 *N* AgNO₃ and 0.05 *N* and 0.1 *N* thiocyanate, depending upon the quantity of halogen to be determined.

For use with this method, an electrically heated multiple and continuous bomb furnace was designed and constructed. This furnace, which will be described elsewhere in detail by W. A. Van Winkle, consisted in brief of six 5 cm. iron pipes, each about 15 meters in length, bound together in an upright bundle by 3 iron bands, and heated by several well insulated coils, which surrounded the lower half of the bundle, as well as by a heating element placed at the base, and one in the center of the bundle, the whole encased in a box of 12 mm. transite asbestos board. By means of pulleys suspended overhead from a framework, six 32 mm. counterpoised iron pipes, or bomb containers, could be lowered into the heated zone of the 5 cm. pipes. Thus, 6 bombs could be introduced independently into or withdrawn from the furnace, and the latter could be operated continuously, since with the upper half of the furnace not directly heated the bombs could be lowered or raised gradually, without a sudden change of temperature. Four thermometers, permanently installed at different heights, together with various permutations of electrical connections, facilitated the easy maintenance of satisfactory temperatures.

Description of the Apparatus Used with Volatile Substances.—This apparatus is illustrated in Fig. 1. We wish to emphasize at the start that with the use of several Bunsen burners, with wing tops set lengthwise of the combustion tube as shown in the figure, and employing the hottest blue flame possible, it was easy to maintain a temperature of nearly 1000° ,

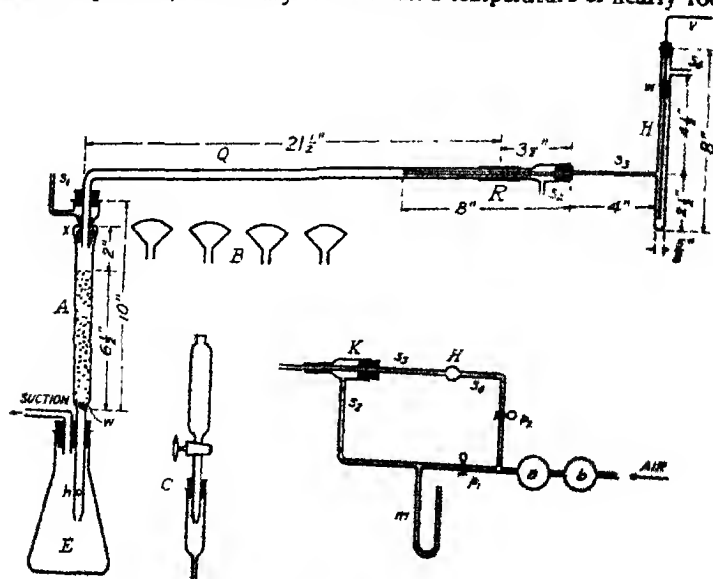


Fig. 1.

especially if an inverted V-shaped reflector of asbestos board were suspended about an inch above the tube.

The sample holder *H* was a Pyrex test-tube, 200 × 16 mm., provided with two side arms of one mm. bore, one, *S*₄, for the entrance of air, and the other, *S*₃, for the exit of air mixed with volatilized sample, this mixture being discharged into the combustion tube far beyond the rubber connection which held the glass adapter *K* against the quartz combustion tube. The glass rod *V* was carefully worked downward through the rubber stopper to break the small, glass sample bulb at the bottom of the holder. To protect the rubber stopper of the holder from attack by the organic substance a tightly fitting plug of glass wool was placed just below the side arm *S*₄.

A washing bottle containing conc. sulfuric acid and a soda-lime tower used to insure the introduction of pure air, are represented in the figure by *b* and *a*, respectively; *m* is a water manometer. Pinchcocks are indicated by *P*₁ and *P*₂. By means of small rubber tubing, *b*, *a*, *S*₄, *S*₂, and *m* were connected up as shown.

The combustion took place in a 60 cm. quartz tube,¹ *Q*, of 6 mm. bore, which was slightly inclined towards, and extended down into the absorption apparatus *A*. Any bromine or iodine condensing near the exit of the tube was later washed over into the absorption vessel, by removing the rubber stopper of *K*, and introducing water into *Q*, slight suction being maintained the while.

The absorption vessel *A* was a piece of glass tubing, 25 cm. long and of 25 mm. outside diameter, into which the absorbing solution continuously flowed through *S*₁. About 38 mm from the upper end the tube was constricted in such a way as to direct the solution towards the combustion tube and cause it to flow down the outside of the latter and drip off its end. Glass wool, packed in the constricted area and also wrapped loosely over the end of the combustion tube, was kept moist by the absorption liquid and thus effectively prevented any loss of halogen by contact with the rubber stopper above. At *w* there was placed a thin layer of glass wool, and above this a 15 to 18 cm. column of sea sand, previously digested with alkali and acid. The extension tube leading into the 500 cc. Erlenmeyer flask *E* had a small perforation, *h*, about an inch above its lower end, which allowed the residual gases to escape and the liquid to drop smoothly from the end of the tube. A small dropping funnel containing 25 cc. of sodium hydroxide solution, 10 cc. of sodium sulfite solution, and about 15 cc. of water, was supported so that the adapter *C* could be connected readily to the side arm *S*₁ by a short length of rubber tubing. The dropping of the liquid from the stem of the funnel,

¹ While a tube of transparent quartz is to be preferred, it was not necessary, both

constricted at the end to about 2 mm., afforded an indication of the rate of flow of the alkaline sulfite solution into the absorption apparatus.

A guard bottle (not shown in the figure), with an entrance tube of 3 mm. bore, and containing water, to serve as a bubble counter, was placed between the Erlenmeyer flask and the suction pump.

Procedure for Carrying Out the Combustion and Absorption.—About 0.25 g. of material to be analyzed was weighed out in a small, sealed bulb, and placed in the lower end of the holder, ready to be liberated at the proper time by breaking the bulb. The apparatus was then set up and adjusted as described, with the absorption solution in the dropping funnel, an asbestos shield to protect the absorption tube and its rubber stopper from the heat of the burners, and an inverted V-shaped asbestos heat-reflector; and the burners were lighted and adjusted. The pinchcocks P_1 and P_2 were opened the water pump and the flow of the absorption solution started from C (the sand in A should become thoroughly soaked with this liquid, before it is reached by the products of combustion). The suction was so adjusted that bubbles passed the counter at the rate of 200 per minute, and the cock of the dropping funnel so that the liquid ran at the rate of 20 to 30 drops per minute. This kept the sand well soaked with fresh reagent.¹ The pinchcock P_2 was then tightly closed, but P_1 left wide open, and the bulb holding the sample was broken. If, after a couple of minutes, no fog appeared above the sand, the pinchcock P_2 was opened slightly; in this way there was no danger of carrying an excess of the volatile sample into the combustion tube. It was necessary that the manometer should always show a negative pressure within the apparatus, of 2 to 6 in. of water. By closing P_2 at any time, the change in level of the liquid gave a rough indication of the relative volumes of air flowing through the two entrances of the combustion tube.

With a substance like ethyl bromide, boiling at 38.4° , it was unnecessary to warm the holder until near the end, when a free flame was cautiously applied to volatilize the small quantity of liquid usually held within the capillary of the sample bulb. Less volatile substances required a gentle warming of the holder at 10 to 30° below their boiling points. In all cases, after once regulating the combustion so that a slight fog continuously hovered above the sand in the absorption vessel, very little attention was required until near the end of the operation.²

¹ If, towards the end, it appeared that not enough solution was left to last out the run, some water was added; the reagent was sufficiently concentrated to permit the addition of 1 to 2 parts of water.

² Sometimes a small blue flame appeared at the end of the capillary side arm S_1 . It was then advisable to close down P_1 , and to open up P_2 , and, in addition, if the holder was being warmed, to withdraw this source of heat. In the preliminary experiments with this apparatus, a much shorter capillary side arm, S_2 , was used, until in one instance the small blue flame flashed back, and the holder broke. The substitution of a holder with a 30 cm. side arm prevented further trouble from this.

When no further fog appeared above the sand, a free flame was applied to the holder, and the latter gradually heated until well above the boiling point of the substance. The burners were then turned out, the asbestos reflector and shields and the apparatus allowed to cool without discontinuing the suction. Within about 10 minutes, the contents of the combustion tube were rinsed into the absorption apparatus by means of a stream of water introduced through the adapter K. The absorption train was then disconnected, and the end of the combustion tube similarly washed, inside and out. Any reagent still in the dropping funnel was allowed to run rapidly through the glass wool into the absorption apparatus, and the latter was washed with a few small portions of hot water, the sand being sucked nearly dry after each addition of liquid.¹ The volume of liquid in the flask was then about 175 cc. It was cooled, if warm, 25 cc. of dil sulfuric acid added, and the excess of sulfur dioxide completely oxidized with the least possible quantity of permanganate solution. The halogen was then determined by the Volhard method, as already described.

Analyses of Several Volatile Compounds.—Analyses of 12 volatile compounds, with the apparatus shown in Fig. 1, are recorded in Table I. Under Time, is given the number of minutes from the breaking of the sample bulb to the end of the combustion, including the final washing of the apparatus, and the tests for complete washing. In a few cases there was a failure to record the time, and in several the time noted is excessive, because, owing to the smoothness of the combustion, the operation was not closely watched, and more time than necessary was consumed.

Comparative analyses of the Carius method are recorded in the same table. The values obtained by combustion will speak for themselves; as compared with the Carius values, they were obtained with exceeding convenience and ease.

TABLE I.

Combustion				Carius		
No	Sample G	Time Min.	Halogen %	No	Sample G	Halogen %
Ethyl bromide, C_2H_5Br (impure), b. p. of pure substance, 38.4° ; Calc., 73.33% Br.						
1	0.3106	70	72.35	6	0.2479	72.24
2	0.3200	85	72.36	7	0.2244	72.07
3	0.2783	30	72.52	8	0.3027	71.67
4	0.3011	30	72.31	9	0.3223	72.34
5	0.2747	25	72.49	10	0.3370	71.78
Mean, 72.43				72.09		

¹ In the case of iodine compounds, some iodine always solidifies in the end of the combustion tube, but this is without harm. When the tube is washed out, and the reagent remaining in the dropping funnel is run into A, the crystals of iodine are readily dissolved and carried into it.

TABLE I (continued).

Combustion				Carius		
No.	Sample G.	Time Min.	Halogen %	No.	Sample G.	Halogen %
Chlorobenzene, C_6H_5Cl (pure); b. p., 132° ; Calc., 31.52% Cl.						
11	o 3350	90	31.28	17	o 2304	31.17
12	o 2720	90	31.65	18	o 1982	31.26
13	o 2579	115	31.76	19	o 2721	31.75
14	o.2821	70	31.47
15	o 3034	95	31.70
16	o 3399	80	31.79
Mean, 31.61						31.39
Ethyl iodide, C_2H_5I (impure); b. p. of pure substance, 72.2° ; Calc., 81.34% I.						
20	o 4522	67	81.47	22	o 3028	81.47
21	o 4074	98	81.48	23	o 4750	80.90
..	24	o 2708	81.20
Mean, 81.48						81.29
Bromobenzene, C_6H_5Br (pure), b. p., 157° ; Calc., 50.90% Br						
25	o 2520		51.01	28	o 3826	51.23
26	o 3147		50.93	29	o 3632	51.26
27	o 2802	120	50.83			...
Mean, 50.92						51.24
Allyl bromide, C_3H_5Br (impure); b. p. of pure substance, 70° ; Calc., 64.57% Br. (Sample difficult to get into bulb without decomposition)						
30	o 2345	120	62.87	33	o 2141	61.02
31	o.2431	110	62.56	34	o 2252	61.70
32	o 2342	120	63.61	35	o 2842	62.12
Mean, 63.01						61.61
Ethylene chloride, $C_2H_4Cl_2$ (pure); b. p., 83° ; Calc., 71.71% Cl.						
36	o 2688	90	71.66	39	o 2773	71.68
37	o 2868	120	71.68	40	o 2414	72.04
38	o 2521	120	71.82
Mean, 71.72						71.86
Butyl bromide, C_4H_9Br (impure); b. p. of pure substance, 100° ; Calc., 58.34% Br.						
41	o 6136	128	58.16	44	o 2429	58.71
42	o 3231	58	58.14	45	o 2937	58.50
43	o 4751	123	58.11
Mean, 58.14						58.60
Benzal chloride, $C_7H_5Cl_2$ (impure), b. p. of pure substance, 212° ; Calc., 44.05% Cl.						
46	o.2963	90	44.51	50	o.2588	44.89
47	o.2332	90	44.41	51	o.2676	44.28
48	o.3049	75	44.47
49	o.2129	...	44.56
Mean, 44.40					

TABLE I (continued).

Combustion
Carius

No.	Sample. G.	Time Min.	Halogen %	No.	Sample. G.	Halogen. %.
Carbon tetrachloride, CCl ₄ (pure); b. p., 78°; Calc., 92.20% Cl.						
52	0.2494	106	91.92	54	0.2321	92.50
53	0.2614	93	91.37	55	0.2805	92.02
..	56	0.2208	91.94
..	57	0.2813	92.63
Mean, 91.64				92.54		
Chloroform, CHCl ₃ (impure); b. p. of pure substance, 61°; Calc., 89.02% Cl.						
58	0.2747	90	88.83	60	0.2430	88.28
59	0.2840	85	88.64	61	0.2485	88.20
.	62	0.2292	88.76
..	63	0.2449	88.48
..	64	0.2494	88.23
.	65	0.3004	88.39
..	66	0.3189	88.44
Mean, 88.74				Mean, 88.40		
Ethylene bromide, C ₂ H ₄ Br ₂ (impure); b. p. of pure substance, 129°; Calc., 85.09% Br.						
67	0.3934	180	84.51	71	0.2800	84.45
68	0.2013	145	84.45	72	0.2955	84.59
69	0.2114	95	84.27
70	0.2178	105	84.41
Mean, 84.41				84.52		
Chloropicrin, CCl ₃ NO ₂ ; b. p. of pure substance, 113°; Calc., 64.72% Cl.						
(An old sample in sealed tube prepared at Johns Hopkins University by R. W. Hale, Jr., and furnished through the Bureau of Mines.)						
73	0.3046	155	64.55	77	0.3413	64.14
74	0.1819	95	64.77	78	0.3448	64.47
75	0.2057	63	64.47	79	0.2946	64.53
76	0.2235	68	64.50	80	0.2342	64.60
Mean, 64.57				64.44		

The Analysis of Substances Containing More than One Halogen.—

As has been pointed out by W. M. Deln,¹ any two halogens in a binary mixture of halides may be calculated from the weight of the mixed silver salts, together with their silver equivalent as determined by the Volhard method. The possibility was studied of obtaining the necessary data for determinations of this class, by the combustion of the sample, followed by the determination in the one sample, of the two values indicated. But, although preliminary experiments gave promise of success, and the titration data obtained concerning the silver excess were very consistent, and probably correct, it was soon found that great difficulty would be encoun-

tered in the previous precipitation of the silver halides alone, for weighing, because the absorption solution in passing through the sand takes up silica, contaminating the silver halide precipitate. Solutions of pure sodium hydroxide and sulfite, prepared from metallic sodium, were also tried; but the quantity of silica obtainable from the acidified absorption solution, while somewhat less in amount, was still appreciable.

In the best of indirect methods, the analytical data must be exceedingly accurate if large errors are not to be introduced in the calculations; and, while in the present case a satisfactory solution of the difficulty might possibly be worked out, the matter was dropped for lack of time.

The Analysis of Difficultly Volatile Substances.—The results obtained with easily volatile substances led to a desire to apply the method to more difficultly volatile, or even to non-volatile, substances. A sample of material already analyzed by the Carius method was first studied. The apparatus at first used was that shown in Fig. 1; but it was found that the substance charred upon heating the holder, tarry material condensed in the side arm leading into the combustion tube, and it was impossible to volatilize this without burning the rubber connection and the stopper.¹ Nevertheless, success was indicated, provided an apparatus could be devised which would permit the burning of the condensed tarry material.

Accordingly, the apparatus was modified as shown in Fig. 2. The holder and combustion tube consisted of one piece of transparent quartz tubing, to which were fused the 2 mm. side arms S_2 and S_4 , also of transparent quartz. A and B are top and side views, with lengths given to scale, and C is a diagrammatic sketch showing the connections of S_4 , S_2 , m , b , a , and the oxygen tank T. When in position for a combustion, the holder was not vertical in this case, but was inclined at an angle of 20° to the horizontal. In the case of solids, a boat was slid into the position shown; and the sample on melting ran to the bottom of the holder. In the case of liquids, a small sealed bulb was used, which was broken as already described; or, if the liquid was non-volatile, it was weighed out in a small quartz tube, which was slid into the holder.

The combustion was carried out as already described, but during combustion the aspiration was somewhat slower; with the introduction of oxygen, less residual gas passed through the absorption apparatus. In general, the pinchcock P_1 remained closed during the combustion, only air passing via P_2 , and oxygen via P_3 . Two or three times as much oxygen as air was used, the latter passing at the rate of about 100 small bubbles per minute. It was necessary that fog should form continuously above the sand in the absorption vessel, but should not become dense; this con-

¹ In spite of these drawbacks, 4 determinations gave values ranging between 48.63 and 49.35% of Br, for a substance with a theoretical content of 50.29% (cf. Table II, which contains the final work

dition depended largely upon the rate of aspiration, but also upon the rate at which oxygen was introduced. If the latter was slow and the former excessive, there was danger of charring. It was very easy, however, to regulate the flow of air and of oxygen, so that the sample volatilized and burned smoothly.

These difficultly volatile substances required the direct heating of the holder; the initially small and steady flame was placed below the point midway between the plug of glass wool, *w*, and the entrance of the combustion tube. If a fog failed to appear shortly in the absorption vessel, the flame was increased, and if that did not suffice, the holder was covered below the flame with an inverted V-shaped asbestos reflector. Then, if the fog still did not materialize, the flame was gradually moved towards this reflector. But it was necessary to avoid charring the material, and thus setting free combustible gases too rapidly. Once having made the proper adjustments, the combustion

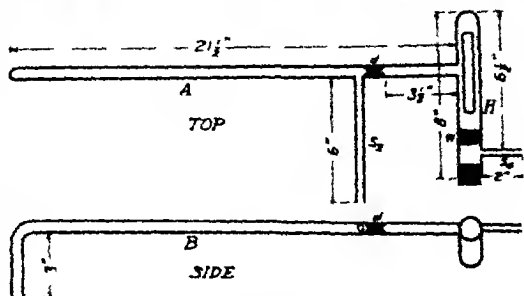


Fig. 2a

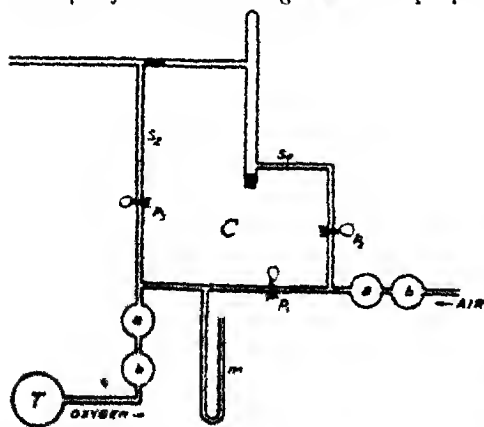


Fig. 2b.

proceeded smoothly, without much attention. Toward the close, the lower end of the holder was always coated with carbon. After heating the end carefully for a few minutes, with only air passing through *H*, the pinchcock *P*₁ was opened and *P*₂ closed. This let in pure oxygen, which readily burned off the carbon. The same applied to the heated deposit between *H* and *d* in the combustion tube. If a small deposit was found in the side arm *S*₄, it also was burned off. The valve of the oxygen tank was then closed, *P*₁ and *P*₂ opened, the 4 burners turned out, and the asbestos boards and the rubber connections of *S*₄ and *S*₅ removed. As soon as the apparatus was almost cool, the rubber stopper, glass wool and boat were removed from *H* and then washed at

absorption train. Finally, the stopper in H was replaced, and the whole apparatus steamed out by boiling off the water remaining in the holder and combustion tube. From this point, the procedure was that already detailed.

In the following tables, when no Carius determinations are given, the materials were considered especially pure, and also time was lacking. Again the results speak for themselves.¹

TABLE II.*

p-Bromo-*o*-(β - γ -dibromopropyl) phenylbenzoate, Calc., 50.29% Br.

Combustion				Carius.		
No.	Sample, G.	Time Min.	Br %	No.	Sample, G.	Br. %.
1	0.2441	95	50.00	3	0.2442	50.10
2	0.2451	60	49.98	4	0.2955	50.02
Mean, 50.04				50.06		

* The sample of material for this work was kindly furnished by Mr. V. L. Harnack, who had previously carried out one Carius determination. Having dried his precipitate in a Gooch crucible for one hour at 110°, he obtained a value of 50.23% Br. In all instances, in this investigation, however, the Gooch crucibles were dried at 130° (first empty, and then with precipitates) to constant weight.

TABLE III.*

Material	Properties.	No.	Sample G.	Time Min.	Halogen. Found %	Calc. %.
<i>p</i> -Bromophenyl- β -bromoallyl ether.....	B. p., 171° at 22 mm	1	0.3194	130	54.06	...
		2	0.2998	165	54.51	54.76
Hexachlorobenzene.....	M. p., 229°	3	0.2431	80	74.60	..
	B. p., 326°	4	0.2484	75	75.01	74.73
<i>m</i> -Iodobenzoic acid	5	0.3776	100	51.09	...
		6	0.3706	105	50.98	50.98
<i>m</i> -Chloro-nitrobenzene.....	M. p., 44.4°	7	0.2800	75	22.70	...
	B. p., 235.6°	8	0.3167	70	22.52	22.51
<i>p</i> -Bromoaniline.....	M. p., 66.4°	9	0.3198	95	46.47	46.18
	B. p., decomp.					

* The material used in the first two determinations was kindly furnished by Dr. S. G. Powell. By a Carius determination, he found 54.1 and 54.4% Br. The other substances were imported.

In conclusion, it is desired to acknowledge the patience and skill of Mr. Paul Anders, the departmental glass-blower, who made all the glass and quartz apparatus used throughout the investigation.

Summary.

1. A simple, rapid, easily executed, and reliable combustion method for the quantitative determination of chlorine, bromine, or iodine in vola-

¹ This style of apparatus can of course be used with volatile substances. With the ethylene chloride previously analyzed, the following values were obtained: I.

tile organic substances has been developed. No catalytic agent is used. The material, volatilized with air, is drawn through a heated quartz tube; the combustion products are absorbed in alkaline sodium sulfite solution; the excess of sulfite is oxidized; and the halogen is determined by the Volhard volumetric method.

2. With some modification of the apparatus, and with the partial use of tank oxygen, the method is equally applicable to non-volatile organic materials.

3. The method is a general one for the determination of halogen in organic compounds; and, in our opinion, it yields to none in accuracy of results or in ease and convenience of execution.

SEATTLE, WASH

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT OF SOLUTION AND THE PARTIAL MOLAL HEAT CONTENT OF THE CONSTITUENTS IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

BY MERLE RANDALL AND CHARLES S. BISSON.

Received November 28, 1912

In order to calculate the free energy of a reaction at one temperature, when the free energy at another temperature is known, we must first obtain the value of ΔH , the increase in heat content accompanying the reaction.¹ This quantity, is defined as the difference between the heat contents of the substances formed and the heat contents of the substances disappearing. For pure substances, ΔH is identical with the negative of the heat of reaction as ordinarily measured. In case one or more of the substances involved in the reaction occurs in solution, we must use, obviously, not the molal heat content, h , of the pure substance, but the heat content of the substance when in solution at the given concentration. This quantity \bar{h} is the partial molal heat content, and is defined as the increase in the heat content of a large amount of the solution at the given concentration when one mol of the substance is added to it.

It is not possible to determine the absolute value of h or \bar{h} for any substance, for we can measure only the difference ΔH between the heat content of the substances appearing and those disappearing in a reaction. However, when no ambiguity will result, we have found it convenient, at a given temperature, to call the value of ΔH , when a substance is formed from the elements in their standard state at the same temperature, the molal heat content or the partial molal heat content of the substance. It is in this sense that these quantities are generally used in this paper, and when so used will always be symbolized by ΔH .

and \bar{H} will be reserved for the absolute molal heat content and the absolute partial molal heat content of the substance.

From the results of the present investigation we have been able to calculate ΔH for the constituents of aqueous solutions of sodium chloride.

Before proceeding further it will be convenient to define a number of quantities related to H and \bar{H} , and to consider which of these related quantities have been used by the various investigators who have measured heats of solution and of dilution.

If we consider the reaction, $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) = \text{NaCl}(0.1 M)$ the partial molal heat content, ΔH (NaCl in $0.1 M$), is the heat absorbed when one mol of sodium chloride is formed from its elements and dissolved in such a large volume of solution that the concentration remains unchanged. The *partial molal heat of solution* of sodium chloride in $0.1 M$ solution, $\text{NaCl}(s) = \text{NaCl}(0.1 M)$, is $\bar{H}(\text{NaCl in } 0.1 M) - H(\text{NaCl})$. Similarly the *partial molal heat of solution* of sodium chloride in its saturated solution is $\bar{H}(\text{NaCl sat.}) - H(\text{NaCl})$. The *partial molal heat of dilution*, $\text{NaCl}(1 M) = \text{NaCl}(0.1 M)$, is $\bar{H}(\text{NaCl in } 0.1 M) - \bar{H}(1 M)$.

Of equal importance with the partial molal heat content of the solute is the partial molal heat content of the solvent. These quantities can be defined in terms of each other by the familiar equation,

$$d\bar{H}(\text{solute}) = - \frac{N(\text{solvent})}{N(\text{solute})} d\bar{H}(\text{solvent}) \quad (1)$$

where N represents the mol-fraction. The partial molal heat content of the water in $0.1 M$ NaCl , $\bar{H}(\text{H}_2\text{O in } 0.1 M \text{ NaCl})$, is the increase in heat content when one mol of water is added to such a large quantity of solution that the concentration remains unchanged. And, as above, we have the important quantity, $\bar{H}(\text{H}_2\text{O in } 0.1 M \text{ NaCl}) - H(\text{H}_2\text{O})$, the partial molal heat of solution of water in $0.1 M$ NaCl .

The molal heat content of the solution is defined in terms of the partial quantities,

$$H(\text{solution}) = N(\text{solute})\bar{H}(\text{solute}) + N(\text{solvent})\bar{H}(\text{solvent}). \quad (2)$$

For a given pure substance it is possible to determine directly the value of the heat content ΔH , but $\bar{H} - H$ has never been measured directly. Rümelin¹ obtained values which approximated $\bar{H} - H(\text{H}_2\text{O})$ for water in concentrated solutions of sodium and potassium chlorides by adding in a calorimeter small amounts of water to large amounts of solution. The partial molal heat content of sulfuric acid was determined by Brönsted,² who discussed the relation between this quantity and the heat of

¹ Rümelin, *Z. physik. Chem.*, 58, 449 (1907).

² Brönsted, *ibid.*, 56, 645 (1906); 64, 641 (1909); 68, 693 (1910). Brönsted calls the heat of solution and the partial molal heat content the integral and differential heats of solution. The temperature of his calorimeter was not stated.

solution. He also determined the heat of solution of sodium chloride at several concentrations.

While this investigation was in progress MacInnes and Braham¹ determined the value for $\bar{h} - h$ for water in aqueous solutions of ethyl alcohol by adding varying small amounts of water to large amounts of the alcohol solution. The values of the heat obtained per mol of water added when plotted as ordinates and the quantity of water added as abscissas gave approximately a straight line. The true value of $\bar{h} - h$ is the intercept of this straight line upon the ordinate axis.

Berthelot and Thomsen and others have determined the *heat of solution* of a large number of substances by adding the substances to pure water. This quantity is of little use in thermodynamic calculations. In those cases in which the *heat of solution* of substances has been determined for a series of dilutions, $\bar{h} - h$ may be calculated by the method used by Lewis.²

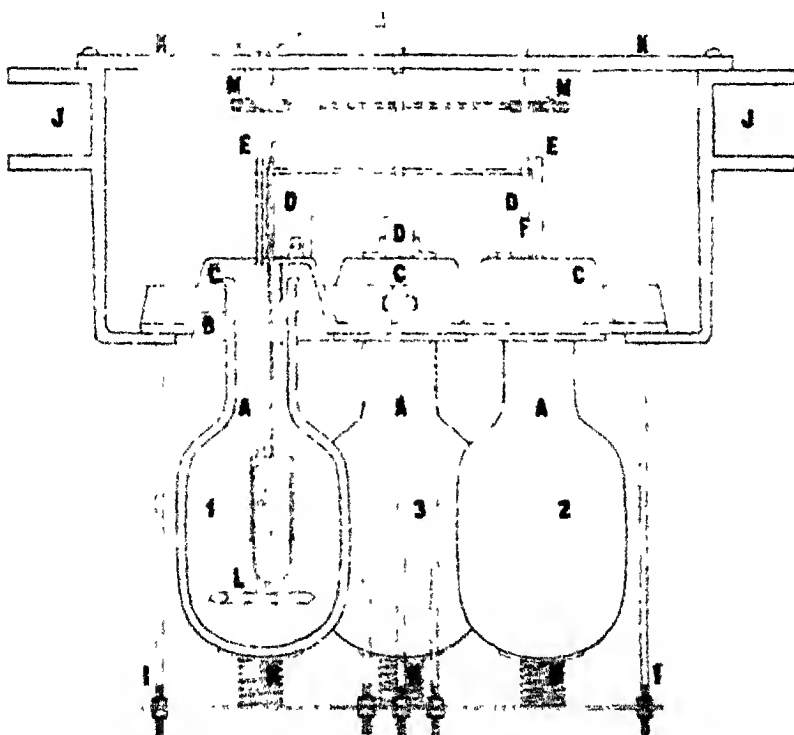


Fig. 1.—Twin vacuum jacketed calorimeters. Elevation.
Scale: 1 cm. = 5 cm.

¹ MacInnes and Braham. *Trans. Faraday Soc.* 36, 297 (1940).

The Calorimeter.—Our apparatus¹ consisted essentially of twin calorimeters (Fig. 1) completely enclosed in a constant temperature air jacket (Fig. 4), a 50-junction differential copper-constantan thermoelement, and a sensitive potentiometer. A third calorimeter and a 20-junction thermoelement also formed a part of the apparatus. These were intended primarily to be used in connection with another investigation. It will be desirable to describe the entire apparatus, as the auxiliary vessel and thermoelement were used in the calibration of the main thermoelement.

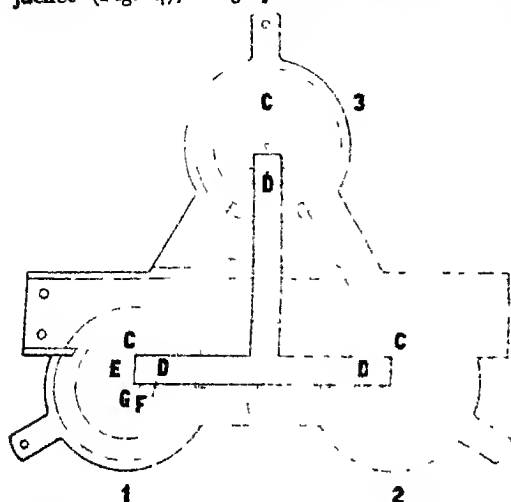


Fig. 2.—Twin vacuum jacketed calorimeters Plan
Scale: 1 cm. = 5 cm.

the approximate heat leak determined. Three flasks, A A A, (Figs. 1 and 2), with like heat leaks were selected. These were fitted by means of large rubber stoppers, B B B, into the caps, C C C. These caps were of cast brass and formed a part of the framework of the calorimeter unit. The interiors of the caps were highly polished, then silver plated and again polished. In the tops of the caps were openings for the thermocouple D, and tubes E F G for the passage of the stirrer, electric leads, upsetting device, etc. The joint between the thermocouple and the cap was made tight by means of rubber packing. The flasks were held in place by means of the supporting springs, H H H. These were in turn held in position by means of framework I I, which was attached to the castings C C C. The whole calorimeter unit was supported upon brackets J J. The rod K served as a brace and as a support for the stirrers M L. The stirrer L consisted of a glass T-tube fitted with tips of rubber tubing. A hole was blown in the stirrer shaft just below the level of the liquid in the calorimeter vessel, and just above this point the tube was sealed to the glass rod which was, in turn, joined to a steel shaft at E by means of a bit of rubber tubing. The three stirrers were driven at a uniform speed of about 150 R. P. M. by means of a chain and sprockets, M M M.

¹No. 322 F, one quart Carafe Filler, Vacuum Specialty Co., Meriden, Conn. These vessels have the desired shape and are manufactured by the same process.

The dilution cup N (Fig. 3) was constructed from a very thin-walled glass test-tube which was cut off to the proper length. Short platinum wires, about 0.5 mm. in diameter, were sealed in at A, and cut off about 3 mm. from the side of the tube. The stirrup was forged from No. 16 nichrome wire and then gold plated. A small piece of platinum wire C prevented the cup from tipping in that direction. The opposite side of the dilution cup rested against the thermoelement D. When it was desired to mix the contents of the dilution cup with those of the calorimeter, the handle F attached to the stirrup was turned through 90°, which allowed the tube N to upset, after which it was raised into the neck of the flask. In this manner it was possible to make the dilution with certainty

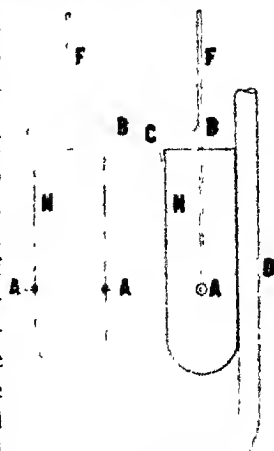


Fig. 3 Dilution cup.
Scale: 1 cm. = 2.5 cm.

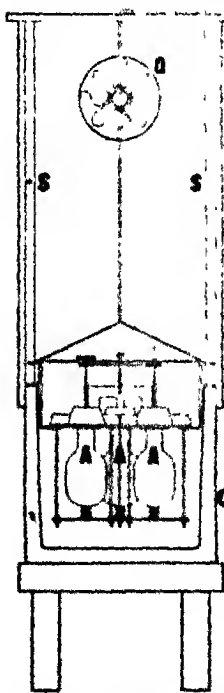


Fig. 4—Twin calorimeters in constant temperature

and without stopping the stirrer L.

The calorimeter unit, consisting of the 3 calorimeters, their supporting framework and stirrers, were mounted in a constant temperature jacket, as shown in Fig. 4. This consisted essentially of one of the standard cast iron water thermostats O 36" X 18" X 18", as used in this laboratory. This thermostat was well stirred, well lagged and kept constant to 0.01°. Above this was constructed a wooden thermostat, P, of 1/2" matched lumber. The air was stirred by means of an ordinary 8" desk fan, Q, was heated by means of lamps, and was regulated to 0.02° by means of a relay and a brass-rubber thermal regulator. The operation of the dilution cup was accomplished through small openings covered with canvas in larger doors which gave access to the calorimeter. The operating position of the calorimeter unit was as shown in Fig. 4. It was counterbalanced by means of the weight R and was raised vertically along the guides SS for convenience in assembling.

The main thermoelement D consisted of 50 junctions of No. 36 double silk covered copper wire soldered to No. 30 double silk covered com-

wire was carefully tested by the method of White.¹ The junctions were insulated by means of cellulose acetate, the couples bundled, and the wire held in place by wrapping the bundle with a single layer of silk binding tape. Seven No. 24 double, silk-covered, copper leads were brought out from the thermocouples and connected to non-thermo-electric binding posts² mounted on hard rubber. Four of the leads divided the main thermocouple into 2 independent 25-junction elements, a fifth divided one of the 25-junction elements into 10- and 15-junction elements, and the last 2 served the 20-junction auxiliary element. The

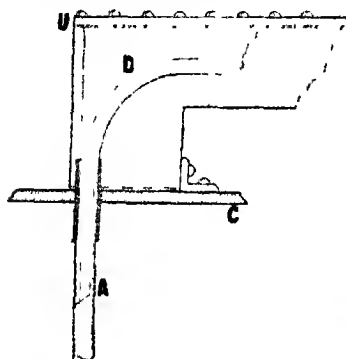


Fig. 5—Detail of thermocouple mounting. Scale 1 cm. = 2.5 cm.

thermoclements, after being bound and taped into shape, were placed in the brass trough-shaped mounting shown in Figs. 1 and 2, a detail of which is shown in Fig. 5. Thin glass protecting tubes partly filled with naphthalene at a temperature just above its melting point were put in position as shown. The trough and the remaining space in the glass tube were then completely filled with paraffin and the paper gasket and brass cover U put in place. The lead wires were then soldered to the copper binding posts, the copper tube and terminal box completely filled with paraffin,

and the hard rubber block carrying the binding posts fastened in place. With a difference of temperature of 3° between Calorimeters 1 and 2 no observable electromotive force has ever been observed when the two 25-junction elements were opposed. In constructing the couple and in designing the mounting extreme care was taken to avoid making sharp bends in the wire or introducing strains due to bending the bundle. The use of silk tape in binding greatly facilitated the careful handling of the thermocouple. The satisfactory performance of our thermocouple is in large measure to be attributed to the careful observance of the above precautions and to the rigid mounting employed.

Our potentiometer has already been described.³ The system was shielded as suggested by White.⁴ Parallel copper wires were supported on a wooden framework and soldered to the various units of the shield and to the main casting C C C of the calorimeter. Between these wires, glass tubes, the surfaces of which were heavily paraffined, were supported

¹ White, *THIS JOURNAL*, 36, 2292 (1914).

² Randall, Bichowsky and Rodebush, *ibid.*, 38, 1266 (1916).

³ White, *ibid.*, 36, 2011 (1914).

by means of wires running through the centers. The lead wires to the potentiometer from the thermocouples, standard cell, galvanometer, etc., were supported upon these paraffined glass rods. The shielding wire, ordinary No. 14 black, weatherproof, copper conductor, was not only an electrical shield, but also an effective mechanical guard and support.

Calibration of Thermocouples.—At the same time as our thermocouples were constructed, Dr. Rodebush, of this laboratory, made two 4-element thermocouples from the stock of wire which we had tested. One of these thermocouples was sent to the Bureau of Standards, where it was compared with their standard resistance thermometer. One end of the couple was placed in melting ice, and the other end in baths at various temperatures between -41° and 50° . Above 0° they found the relation between the electromotive force and the temperature to be given by the following equation with a probable accuracy of 0.005° to 0.01°:

$$E = 163.50t + 0.2030t^2 - 0.000245t^3 \quad (3)$$

Rodebush¹ found that his second 4-element thermocouple was identical with the first. Our 20-junction element was compared with the standardized 4-junction element and found to have an electromotive force exactly 5 times that of the 4 junction element within the limits of the Bureau of Standards equation. For this comparison large Dewar test-tubes were substituted for the Calorimeter Flasks 2 and 3 (Figs. 1 and 2).

The temperature of the water in a third Dewar test-tube which was substituted for Calorimeter No. 1, was kept at approximately 25° , the water in No. 2 was kept constant at approximately 24.5° and 26.5° , and No. 3 was filled with a mixture of ice and water. The temperature of the water in No. 1 was measured accurately by means of the 4-junction element, and that in No. 2 was measured by means of the 20-junction element. The e. m. f. readings of the 50-junction element were taken every minute, those of the 20- and 4-junction elements alternately on the half minute over a period of about 30 minutes, and these readings interpolated to common times.

The following table summarizes the averages of the results of the several series. The second column gives the average e. m. f.s of the 4-junction element, the third gives the averages of the temperatures of Tube 1 calculated from Equation 3, the fourth gives $\frac{1}{5}$ of the average e. m. f.s of the 20-junction element, the fifth the average temperatures of Tube 2, the sixth the average e. m. f.s of the 50-junction element divided by 12.5, the seventh the difference between the sum of the e. m. f.s in Cols. 4 and 6 and those in Col. 2, and the eighth the average value of $\Delta E/\Delta t$ for the 50-junction element as calculated from the individual values of E_{40} and the calculated temperatures.

TABLE I.—MICROVOLTS PER DEGREE FOR THE 50-JUNCTION THERMOELEMENT.

Series.	E_0 M m. v.	t	$E_{20} \times 0.2$ M m. v.	t	$E_{20} \times 0.08$ M m. v.	Difference, M m. v.	$\Delta E_0/\Delta t$ M m. v./deg
1.....	4182.1	24.84	3957.7	23.54	223.4	-1.0	2152
2.....	4187.7	24.97	4439.4	26.32	-250.2	+1.5	2152
3.....	4188.4	24.88	3942.8	23.46	244.9	-0.7	2152
4.....	4200.4	24.99	4480.4	26.55	-272.1	-1.1	2172
5.....	4208.2	24.99	4480.1	26.55	-272.6	-0.7	2174
6.....	4207.5	24.98	4478.9	26.55	-272.4	-1.0	2177
7.....	4188.5	24.86	4519.1	26.78	-331.5	-0.9	2155
8.....	4186.4	24.86	4520.3	26.79	-331.5	+2.4	2152
9.....	4188.8	24.88	4521.6	26.79	-331.2	+1.6	2160
10.....	4192.2	24.90	4526.3	26.82	-333.2	+0.9	2162
11.....	4203.8	24.96	4532.4	26.86	-328.8	-0.2	2171

It would have been very desirable to compare directly the 50-junction element with the standardized 4-element couple, but owing to its peculiar form of mounting we were unable to arrange it alongside the 50-junction element. The direct comparison of the 20-junction with the 4-junction thermoelement showed that these couples were identical. If the 50-junction thermoelement was also identical with the 4-junction thermoelement, the difference shown in Col. 7, Table I, should be zero, provided that the temperatures of the two sets of junctions in each vessel were identical. We will take as the final values for dE/dT those obtained by differentiating Equation 3, by which we obtain 2163 microvolts per degree at 24.5° , 2165 at 25° , and 2167 at 25.5° . These values agree, as would be expected, within the limits of experimental error, with those given in Col. 8 of Table I. Any small error in the value of dE/dT will affect the calorimetric determinations to a much smaller degree.

Heat Capacity of the Calorimeter.—The heat capacity of the calorimeter was determined in the following manner: A weighed amount of water was placed in the calorimeter flask and a constant current passed through a known resistance. The resistance consisted of a coil, of manganin¹ (Therlo) wire, whose resistance was determined by means of a Wheatstone bridge. The current was measured by means of the usual standard ohm coil and potentiometer, and the time (about 10 minutes) by means of a stopwatch. The quantity of water used was varied so that the level of the water corresponded with that used in the dilution experiments. The temperature of the jacket and twin calorimeters was 25° . The change of the e. m. f. of the 50-junction differential element was measured by means of the combination potentiometer. The usual initial and final periods were taken at half minute intervals. The rate of change

¹ This coil had a resistance of 1.951 ohms. It consisted of a coil of No. 26 Therlo wire wound upon mica and enclosed in a flat, copper case which was afterwards silver-plated. The specific heat of the mica (0.388 g.) was taken as 0.208, of the copper

during these periods reached a very constant value which was not greater than $dE/dt = 1.1$ m.m.v. per minute. The results of these experiments are given in Table II. The first column gives the number of the vacuum bulb used, the second the weight of water used, the third the electrical energy added expressed in calories, the fourth the observed change in e. m. f., the fifth the temperature rise, the sixth the total heat capacity of the system, the seventh the heat capacity of the water and the heating coil, and the last the heat capacity of the calorimeter. All weights are reduced to vacuum, one calorie equals 4.182 joules, and the specific heat of the water at 25° was taken as 0.9978.

TABLE II.—HEAT CAPACITY OF VACUUM FLASK CALORIMETERS.

		Wt of H ₂ O G	Energy added Cal	ΔE M m v	Δt	C_p System Cal / deg	C_p Water + coil Cal / deg	C_p Calorim- eter. Cal / deg
L 1	..	800.8	522.0	1345.6	0.6209	840.6	799.2	41.4
L 1.	.	800.8	487.5	1261.0	0.5819	837.8	799.2	38.6
L 1		800.8	540.4	1400.9	0.6465	835.9	799.2	36.7
L 2		800.8	593.9	1518.9	0.7009	847.3	799.2	48.1
L 2		800.8	704.2	1799.3	0.8303	848.2	799.2	49.0
L 2.	..	600.6	677.9	2273.0	1.0489	646.3	600.0	46.3
L 2		600.6	650.8	2183.9	1.0078	645.7	600.0	45.7
L 2	.	900.9	682.7	1566.2	0.7229	944.6	899.7	44.9
L 2		900.9	653.0	1496.1	0.6904	945.9	899.7	46.2
L 2		900.9	668.8	1533.4	0.7076	945.2	899.7	45.5
L 2		800.8	42.86	109.66	0.05068	847.8	799.8	48.0
L 2	...	800.8	44.57	114.26	0.05272	846.6	799.8	46.8

The value for the heat capacity of flask L 1, together with that of the stirrer and thermocouple was taken as 38.9 calories per degree, that for L 2, etc., as 46.0 calories per degree. In the last two measurements only a very small current was passed through the heating resistance, and the temperature rise was very much smaller than in the preceding experiments. It was found that the heat capacity of the flask was, within the limits of experimental error, the same as that obtained in Expts. 3 to 10, in which the temperature rise was nearly one degree.

Specific Heat of Solutions of Sodium and Potassium Chlorides at 25° .—The experimental procedure used in determining the specific heats of these solutions was the same as that employed in determining the heat capacity of the calorimeter flasks, except that the solution was substituted for the pure water. The results are given in Tables III and IV. In each experiment 800.8 g. of solution was placed in calorimeter flask L 2. The first column gives the concentration, the second the energy added expressed in calories, the third the observed change in e. m. f. of the thermocouple, the fourth the

TABLE III.—SPECIFIC HEAT OF SOLUTIONS OF SODIUM CHLORIDE AT 25°.

M	Energy added, Cal	ΔE , M m. v.	Δt	C _p , System Cal./deg.	C _p , Solution Cal./deg.	Specific Heat, Cal./g./deg.
6.20	361.9	1169.6	0.5397	670.5	623.8	0.779
6.17	446.2	1433.8	0.6616	674.4	627.7	0.784
6.20	735.9	2372.5	1.0947	672.2	625.5	0.781
6.20	736.3	2366.5	1.0925	673.9	627.2	0.784
4.04	688.0	2112.1	0.9746	705.9	659.2	0.824
4.03	585.0	1800.9	0.8311	704.0	657.3	0.821

TABLE IV.—SPECIFIC HEAT OF SOLUTIONS OF POTASSIUM CHLORIDE AT 25°.

M.	Energy added, Cal	ΔE , M m. v.	Δt	C _p , System Cal./deg.	C _p , Solution Cal./deg.	Specific Heat, Cal./g./deg.
4.85	655.3	2308.4	1.0655	615.1	568.4	0.710
4.84	618.4	2180.0	1.0060	614.7	568.0	0.710
4.84	715.2	2514.1	1.1602	616.5	569.8	0.712
2.72	723.0	2279.4	1.0517	687.4	640.7	0.801
2.73	724.3	2277.2	1.0508	689.2	642.5	0.803
2.73	703.5	2212.0	1.0210	689.0	642.3	0.803

The mean value of the specific heat in the above tables, together with the data obtained by Thomsen,¹ are given in Tables V and VI. The first column gives the observer, the second the concentrations, and the third the specific heat in terms of the 15° calorie.

TABLE V.—SPECIFIC HEAT OF SODIUM CHLORIDE SOLUTIONS AT 25°.

	Mols./1000 g. H ₂ O.	Sp. H.
R and B.	6.20	0.782
T.	5.55	0.791
R and B.	4.04	0.822
T.	2.78	0.863
T.	1.85	0.895
T.	1.11	0.931
T.	0.553	0.962
T.	0.278	0.978
	0.000	0.9978

TABLE VI.—SPECIFIC HEAT OF POTASSIUM CHLORIDE SOLUTIONS AT 25°.

	Mols./1000 g. H ₂ O	Sp. H.
R and B.	4.84	0.711
T.	3.70	0.761
R and B.	2.73	0.802
T.	1.85	0.850
T.	1.11	0.904
T.	0.555	0.948
T.	0.278	0.970

¹ Thomsen, "Thermochemistry," trans by Burke, p. 162. Longmans, Green and Co., 1908. Thomsen's measurements were made between 18° and 20° and were expressed in 18° calories. His calorie was, therefore, smaller than the 15° calorie which we have used, and his results were 0.1% high. If we assume, however, that the specific heats of sodium and potassium chloride solutions decrease with an increase in tem-

The measurements given in Tables V and VI have been plotted in Fig. 6. All the values fall upon smooth curves except the one for sodium chloride (2.78 *M*), at which concentration the value 0.860 appears to be the best value.

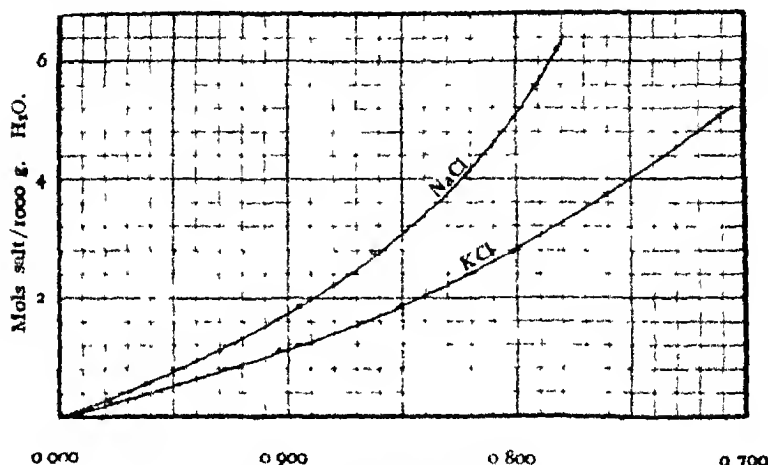


Fig. 6.—Specific heat of solution

If, in calculating the change of the free energy of a reaction with the temperature, ΔH is not constant but is a function of the temperature, then we must know the difference between the heat capacities of the substances appearing in the reaction and those disappearing.¹ If one or more of the substances taking part in a reaction occur in solution, we must use not the heat capacity of the solution, or the heat capacity of the pure substances, but the heat capacity of the substance when in the solution at the given concentration. This quantity, \bar{c}_p , the partial molal heat capacity, is the increase in the heat capacity of a large amount of the solution at the given concentration when one mol of one of the constituents is added to it. If we attempt to evaluate the partial molal heat capacity of the constituents, using the values given in Tables V and VI, and using the method suggested by Lewis,² we find that the value of \bar{c}_p for sodium chloride and for potassium chloride in their dilute solutions is negative. It is zero near 1.5 *M* for sodium chloride and 2.5 *M* for potassium chloride, and is positive at greater concentrations. The above data are sufficiently accurate for the calculation of the results of our calorimetric measurements and for an approximate calculation of \bar{c}_p , especially in the more concentrated solutions.³

¹ See Lewis, *THIS JOURNAL*, 35, 1 (1913).

The Partial Molal Heat of Solution of Water, $\bar{h}-h(H_2O)$, in Solutions of Sodium Chloride.—The measurement of the heat absorbed when water was added to solutions of sodium chloride was carried out as follows: The temperature of the room was adjusted to $24^\circ \pm 1^\circ$, and that of the air thermostat to $25^\circ \pm 0.02^\circ$. The solution and distilled water were brought to 25° in a water thermostat. The Calorimeter Flask 1 was removed from the air thermostat and the required amount of solution quickly weighed into it, and the flask replaced in the air thermostat. Water at 25° was likewise transferred to Calorimeter Flask 2. In some cases it proved convenient to introduce the water into Flask 2 at a temperature slightly less than 25° and to adjust it by means of a small heating coil which was left in the flask during the experiment. Distilled water at 25° was then transferred to the dilution cup (Fig. 3) by means of a calibrated pipet, delivering 24.92 g. of water in Expts. 1 to 52, and 24.96 g. of water in the remaining experiments. When not in use the pipet was kept in the air thermostat. The calorimeter was then assembled, lowered to its operating position, and the stirrers set in operation. The stirrers were allowed to operate for about 4 hours, at the end of which time, if the above precautions were properly observed, the e. m. f. of the 50-junction element would be between 0 and 10 microvolts, and its rate of change would not be greater than 0.5 mm. on the galvanometer scale, which corresponded to 0.05 m.m.v. per minute. In some cases this rate was as small as 0.001 m.m.v. per minute.

If the rate of change of e. m. f. was uniform, the rest point of the galvanometer was taken, then the usual initial period of about 8 minutes, after which the dilution was made as previously described. The rest point of the galvanometer was again determined, the readings of the e. m. f. continued at minute intervals until a constant rate of change of the e. m. f. was again reached, usually between 40 and 60 minutes, when the rest point of the galvanometer was again determined. The curve of the galvanometer deflection against time was then extrapolated to the time at which the dilution was made and the extrapolated value reduced to microvolts. As the greater part of the temperature change occurred during dilute solutions. For this purpose two heating coils of like resistance are connected in series and one of them placed in Calorimeter 1 and the other in Calorimeter 2. The difference in the heat capacities of the two calorimeters can be accurately measured by placing equal amounts of water in the two calorimeters, passing a known current for a given time through the heating coils, and measuring, by means of the 20-junction element, the total rise in temperature of Calorimeter 1, and, by means of the 30-junction thermoelement, the difference in the temperature changes of Calorimeters 1 and 2. In the measurement of the specific heats of the solutions, the water in one of the calorimeters is replaced by solution. From the data obtained in such measurements it should be possible to calculate the values which \bar{c}_p for NaCl and for KCl approach in dilute solutions.

the first 2 or 3 minutes, no large uncertainty in the method of extrapolation can exist.

The results of the experiments are given in Table VII. Col. 1 gives the number of the experiment, the second column gives the initial weight of the solution, the third the initial concentration, the fourth the final concentration, the fifth the specific heat of the final solution taken from the curve given in Fig. 6, the sixth the difference in the initial and final values of the e. m. f., extrapolated to the time of dilution, the seventh the corresponding change in temperature, the eighth the heat absorbed, and the ninth the heat absorbed per mol. of water added. Calorimeter flask L₁ was used in Expts. 1 to 11, and L₂ in Expts. 12 to 59.

TABLE VII.— $\bar{H}(\text{H}_2\text{O})$ IN NaCl — $\bar{H}(\text{H}_2\text{O})$ AT 25°.

No	Wt of solution G.	M Initial	M Final	Sp. H Final solution	$-\Delta E$ M m v	$-\Delta t \times 10^3$	Heat absorbed Cal	Heat per mol H ₂ O Cal.	$\bar{H} - \bar{H}_0$ Cal.
1	790.7	6.12	5.97	0.784	53.62	24.76	16.81	12.15	11.5
2	790.7	5.97	5.74	0.783	59.90	28.39	19.35	13.98	12.9
3	790.7	5.74	5.54	0.791	76.44	33.30	24.15	17.46	...
4	790.7	4.63	4.47	0.811	99.66	46.01	32.22 ^a	22.70	21.8
5	790.7	4.47	4.31	0.815	99.94	46.12	32.43	23.43	23.1
6	790.7	4.31	4.12	0.820	102.43	47.28	33.46	24.18	...
7	790.7	3.99	3.84	0.827	89.98	41.56	29.63	21.42	21.5
8	790.7	3.84	3.69	0.831	97.30	44.94	32.20	23.27	...
9	790.7	3.69	3.54	0.836	91.33	42.18	30.40	21.99	...
10	790.7	3.46	3.33	0.842	78.09	36.80	26.18	18.94	19.4
11	790.7	3.33	3.24	0.845	74.57	34.41	25.05	18.13	...
12	780.7	3.24	3.13	0.848	77.45	35.77	26.08	18.86	19.3
13	780.7	3.13	3.01	0.852	72.91	33.67	24.66	17.84	18.2
14	780.7	3.01	2.90	0.855	69.23	31.99	23.50	16.99	17.3
15	780.7	2.90	2.80	0.858	66.21	30.58	22.54	16.30	16.5
16	780.7	2.80	2.70	0.862	63.88	29.51	21.84	15.80	16.0
17	780.7	2.70	2.60	0.866	61.88	28.60	21.26	15.39	15.5
18	780.7	2.60	2.51	0.869	60.22	27.82	20.76	15.02	...
19	780.7	2.06	1.99	0.889	41.08	18.97	14.45	10.46	10.6
20	780.7	1.50	1.45	0.913	22.83	10.54	8.24	5.96	6.0
21	780.7	1.45	1.40	0.916	22.75	10.50	8.24	5.96	...
22	780.7	0.944	0.912	0.942	10.41	4.81	3.86	2.79	2.8
23	780.7	0.882	0.858	0.944	11.29	5.21	4.20	3.03	3.0
24	780.7	0.425	0.412	0.970	2.00	0.92	0.76	0.55	0.55
25	780.7	3.09	3.00	0.836	72.28	33.38	24.00	17.54	17.7
26	780.7	3.00	2.91	0.838	69.54	32.13	23.15	16.78	...
27	780.7	1.95	1.87	0.891	37.07	17.12	13.07	9.45	9.6
28	780.7	1.87	1.82	0.897	35.68	16.47	12.66	9.16	9.3
29	950.8	6.25	6.00	0.784	42.04	19.43	15.76	11.40	10.9
30	950.8	6.01	5.79	0.785	46.49	21.47	17.44	12.82	12.0
31	950.8	5.99	5.79	0.786	47.93	22.15	18.00
32	950.8	5.79	5.60	0.789	54.36	25.10	20.49	14.82	13.9
33	950.8	5.60	5.40	0.793	61.48	28.40	23.29	16.85	16.3

^a A plot of Expts. 1 to 9 gave a value of 30.53 cal. for Expt. 4. This value was used in calculating heat/mol and $\bar{H} - \bar{H}_0$.

TABLE VII (continued)

No.	Wt of solution, G	M. Initial.	M Final	Sp. H Final solution	$-\Delta E$ M in v	$-\Delta i \times 10^3$	Heat absorbed Cal	Heat per mol H ₂ O Cal	$\bar{H} - \bar{H}_0$ Cal.
34	950.8	5.40	5.21	0.796	65.23	30.14	24.80	17.94	17.5
35	950.8	5.21	5.02	0.800	63.23	29.31	24.15 ^b	18.60	17.9
36	950.8	5.02	4.89	0.802	71.26	32.90	27.36	19.71	19.4
37	950.8	4.89	4.73	0.806	73.35	33.86	28.20	20.40	20.1
38	950.8	4.73	4.60	0.808	76.44	35.30	29.48	21.32	21.2
39	950.8	4.60	4.45	0.812	77.07	35.59	29.82	21.57	21.7
40	950.8	4.46	4.29	0.816	78.45	36.23	30.42	22.01	22.1
41	950.8	4.29	4.15	0.819	76.35	35.24	29.75 ^c	21.78	21.9
42	950.8	4.15	4.00	0.823	76.56	35.35	29.88	21.62	21.6
43	941.8	3.39	3.29	0.843	65.81	30.39	26.19	19.24	19.6
44	950.8	3.29	3.19	0.846	63.66	29.40	25.62	18.88	19.2
45	950.8	3.19	3.09	0.850	61.34	28.33	24.78	18.56	18.8
46	950.8	2.43	2.37	0.874	44.79	20.77	18.67	13.50	13.8
47	950.8	2.37	2.30	0.877	42.69	19.70	17.78	12.86	13.2
48	950.8	1.89	1.84	0.896	28.73	13.26	12.19	18.83	9.0
49	950.8	1.84	1.80	0.897	33.04	15.25	14.04		
50	950.8	1.80	1.76	0.899	26.77	12.34	11.41	8.26	8.4
51	950.8	1.13	1.10	0.931	13.61	6.28	5.09	4.33	4.4
52	950.8	1.10	1.07	0.933	12.94	5.97	5.71	4.13	4.2
53	1000.9	4.31	4.18	0.918	71.06	32.83	28.45	20.40	21.1
54	1000.9	4.18	4.07	0.821	72.16	33.31	28.91	20.87	21.0
55	1000.9	4.07	3.94	0.825	71.63	33.08	28.81	20.80	21.0
56	950.8	3.94	3.82	0.828	73.54	33.97	28.25	20.40	20.6
57	950.8	3.82	3.70	0.831	72.33	33.39	27.93	20.16	
58	950.8	3.70	3.57	0.835	72.00	33.23	27.90	20.15	
59	950.8	3.57	3.44	0.839	65.19	30.20	25.47	18.34	

^b From a plot 25.72 appears to be a more likely value.^c From a plot 30.10 appears to be a more likely value.

The heat absorbed per mol of water added, given in Col. 9, is very nearly $\bar{H} - \bar{H}_0$. However, the amount of water added is not infinitesimal as compared with the amount of solution. In most cases the final solution of an experiment was the initial solution of the succeeding one. In these cases, by combining the results of one experiment with those of the succeeding experiments and making corrections for the additional quantity of water needed to dilute the 25 g. of solution which was removed for analysis, etc., and the additional heat which would accompany this dilution, we obtain the amount of heat which would be absorbed when the original amount of solution was diluted with a little more than 50 g. of water. By combining these results once again with those of the next succeeding experiment, we obtain the quantity of heat absorbed when a little more than 75 g. of water is added to the original amount of the solution. If, then, the amount of heat per mol of water added is plotted as a function of the amount of water added,¹ we may extrapolate and find the

¹ MacInnes and Braham, *This Journal*, 39, 2110 (1917).

value of $\bar{h} - h$ at the initial concentration of the first solution. If the variation of \bar{h} with the concentration is nearly linear over the concentration change considered, the extrapolation is quite satisfactory, otherwise the result is somewhat uncertain. The values of $\bar{h} - h$ are given in the last column of Table VII and are plotted in Fig. 7.

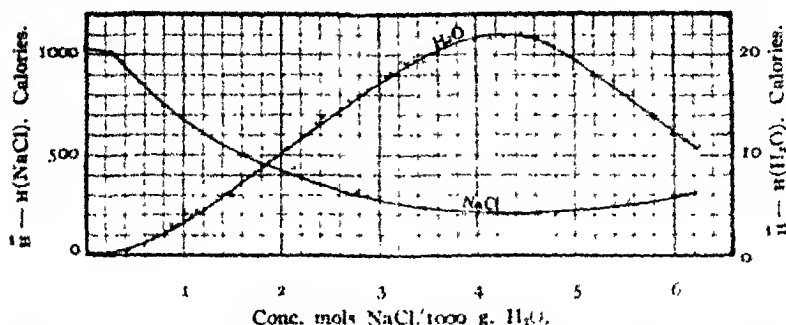


Fig. 7.—Partial molal heat of solution of the constituents in aqueous solutions of sodium chloride.

Besides the values given in this table, we also know that the partial molal heat content of the water will approach a constant value in dilute solutions, namely, the heat content of water. Thus $\bar{h} - h = 0$ at infinite dilution. The values gradually increase, reaching a maximum of about 21 calories at 4.2 *M*, and then decrease to a value of about 11 calories in a saturated solution. The shape of the curve will be discussed further in a later section.

Partial Molal Heat Content of Water in Solutions of Sodium Chloride.

—For liquid water Lewis and Randall¹ have used the value $\Delta h_{230} =$

TABLE VIII.—PARTIAL MOLAL HEAT CONTENT OF WATER IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE

Conc. mol per 1000 g. H ₂ O	$\Delta h(H_2O \text{ in NaCl aq.})$ (Cal)
0.00	—69,272
0.55	—68,271
0.8	—68,270
1.0	—68,269
1.4	—68,266
2.0	—68,263
2.5	—68,268
3.0	—68,255
3.5	—68,252
4.2	—68,250
4.8	—68,251
5.2	—68,254
5.8	—68,258
6.12	—68,261

¹ Lewis and Randall, *THIS JOURNAL*, 35, 1969 (1914).

—68470 cal. This corresponds at 25° to —68272 cal. Combining this value of ΔH_{298} with the values for $\bar{H} - H(H_2O)$ given in the last column of Table VII, we obtain the following values for the partial molal heat content of water in solutions of sodium chloride. The first column gives the concentration and the second the values of $\Delta H(H_2O \text{ in NaCl aq.})$.

Heat of Dilution of Solutions of Sodium Chloride.—The measurements of the heat absorbed when a small amount of saturated solution (6.12 *M*) of sodium chloride at 25° was added to 700 g. of water, contained in flask L, I, were made in the same manner as those described in the previous section. In Table IX the first column gives the final concentration of the solution as determined by analysis, the second the specific heat, the third the weight of saturated solution added, as calculated from the final analysis, the fourth $-\Delta E$, the fifth $-\Delta$, the sixth the heat absorbed in calories, and the seventh the heat absorbed when a solution 6.12 *M*, containing one mol of sodium chloride is diluted to the final concentration, given in Col. 1. The mean of the last 4 measurements gives 606 calories

TABLE IX.—HEAT OF DILUTION OF 6.12 *M* NaCl

<i>M</i> Final	Sp. Heat Cal./g./deg.	Wt. of solution added (g.)	<i>M</i> Final	$-\Delta E$ X 10 ³	Heat absorbed Cal.	Heat/mol NaCl Cal.
0.1792	0.986	29.47	2.12 14	97.96	52.50	621.3
0.1761	0.987	28.95	2.04 51	93.43	79.15	606.4
0.1856	0.9855	30.51	2.14 12	95.80	55.78	609.0
0.1844	0.985	30.31	2.10 94	96.93	52.10	600.8
0.1758	0.9865	28.9	2.2 46	93.45	79.10	607.0

The value obtained above may be compared with that derived by the following method from the values given in Table VII. The values of ΔH are plotted as ordinates and the concentrations, expressed as mols of water per mol of salt, as abscissas in Fig. 8. The heat Q absorbed when

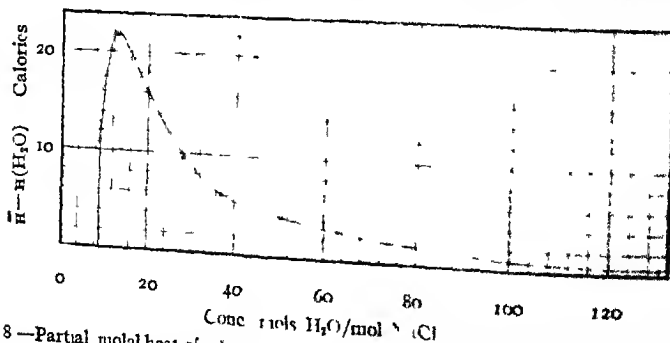


Fig. 8—Partial molal heat of solution of water in aqueous solutions of sodium chloride.

$x_2 - x_1$ mols of water is added to a solution containing x_1 mols of water per mol of solute is given by the equation

$$Q = \int_{x_1}^{x_2} \bar{H} dx. \quad (4)$$

Now the value of this integral is the area under the curve (Fig. 8) between the concentration limits x_1 and x_2 , and the heat of dilution may be found directly by counting squares. The first column in Table X gives the upper concentration limit, mols H_2O /mol NaCl , the second the lower concentration limit, mols H_2O /mol NaCl , the third the same concentration expressed in mols NaCl per 1000 g. H_2O , the fourth the heat absorbed on the dilution of a solution containing one mol of sodium chloride from the upper to the lower concentration, and the fifth the heat absorbed when a solution, 6.12 M NaCl , containing one mol of sodium chloride is diluted to the concentration given in Col. 3.

TABLE X.—HEAT OF DILUTION OF SODIUM CHLORIDE SOLUTION.

$\frac{\text{Mols H}_2\text{O}}{\text{Mols NaCl}}$	$\frac{\text{Mols H}_2\text{O}}{\text{Mols NaCl}}$	$\frac{M}{\text{Mols NaCl}} \frac{1000 \text{ g H}_2\text{O}}{1000 \text{ g H}_2\text{O}}$	Q $x_1 \text{ to } x_2$ Cal./mol NaCl	Q 6.12 M to M Cal./mol NaCl
9.04	10.0	5.55	13.0	13.0
10.0	12.0	4.63	38.2	51.2
12.0	14.0	3.95	43.8	95.0
14.0	16.0	3.47	41.0	136.0
16.0	18.0	3.08	37.6	173.6
18.0	20.0	2.78	34.1	207.7
20.0	22.0	2.52	30.4	238.1
22.0	26.0	2.13	51.2	289.3
26.0	28.0	1.982	20.0	309.3
28.0	30.0	1.850	18.5	327.8
30.0	34.0	1.632	31.4	359.2
34.0	38.0	1.461	26.0	385.2
38.0	50.0	1.110	60.6	445.8
50.0	60.0	0.925	36.5	482.3
60.0	100.0	0.555	80.0	562.3
100.0	150.0	0.370	35.0	597.3
150.0	200.0	0.278	10.0	607.3
200.0	2.0	609.3

The further dilution of a 0.278 M solution of sodium chloride produces only a small heat effect. From a consideration of the probable value of $\bar{H} - \bar{H}$ for water in solution, as indicated by the curve in Fig. 7, we have estimated approximately 2 calories for the heat of dilution from 0.278 M to infinite dilution. The value for the heat of dilution of one mol of sodium chloride from 6.12 M to infinite dilution, namely 609 calories, agrees well within the limits of experimental error with 606 calories, the value given by Table VIII. For convenience in using Table X we will make two small adjustments, calling the heat of dilution from 60.0 to 100.0 mols equal to 77.7 cal., and that from 100.0 to 150.0 mols equal to 34.0 cal. We then have for the values for the heat of dilution of 6.12 M NaCl to 0.555 M , 560.0 cal.; to 0.370 M , 594 cal.; to 0.278 M , 604 cal.; and to infinite dilution, 606 cal.

Heat of Solution of Sodium Chloride.—The heat of solution of sodium chloride was determined by placing small amounts of pure dry sodium chloride in the dilution cup and adding it, as in the previous experiments, to 790.8 g. of pure water. Calorimeter Flask I, 1 was used. The first column of Table XI gives the concentration of the final solution, the second the specific heat of the final solution, the third — ΔE , the fourth — Δt , the fifth the heat absorbed in calories, the sixth the heat absorbed per mol of sodium chloride dissolved, and the last column the sum of the values in the sixth column and the heat absorbed when the solution is further diluted to infinite dilution.

TABLE XI.—HEAT OF SOLUTION OF SODIUM CHLORIDE AT 25°.

M_{Final}	Sp. H. Cal./g./deg.	ΔE Cal./mol.	$-\Delta t$ °C.	Heat absorbed Cal.	Q Cal./mol NaCl	Q in large amount of H_2O .
0.1266	0.9895	266.46	123.0	101.9	1018	1018
0.1297	0.9895	274.71	127.0	105.0	1024	1024
0.1277	0.9895	266.14	123.4	100.9	1009	1009
0.2667	0.9795	572.28	290.1	214.7	1018	1020
0.2597	0.9805	545.31	262.1	208.2	1014	1016
0.4601	0.9640	949.55	439.0	362.2	995	1021
0.5400	0.9630	1096.6	507.0	418.0	979	1023

The mean heat of solution of sodium chloride in a very large amount of water is 1019 calories per mol. Several attempts were made to dissolve larger amounts of solid sodium chloride in water in the calorimeter, and also to dissolve it in varying concentrations, but the temperature equilibrium was established very slowly. The results were erratic and of no value. The same results can, moreover, be directly obtained from the results already given in Table X and XI. The values for the heat of solution when one mol of sodium chloride is dissolved in enough pure water to form solutions of the various concentrations are given in Table XII and plotted in Fig. 9. The ordinates above the line $Q = 413$ cal.,

TABLE XII.—THE HEAT OF SOLUTION OF SODIUM CHLORIDE AT 25°.

M	Mols H_2O / mol NaCl	Heat of solution Cal./mole NaCl	Heat of Solution Cal./1000 g. H_2O
6.12	9.04	413	2528
5.55	10.0	426	2364
4.63	12.0	464	2149
3.47	16.0	549	1905
2.78	20.0	621	1726
2.13	26.0	702	1495
1.632	34.0	772	1260
1.110	50.0	859	954
0.793	70.0	915	724
0.555	100.0	973	540
0.370	150.0	1007	372
0.278	200.0	1017	283
0.0	.	1019	0

which is the heat of solution to form 6.12 *M* solution (saturated solution 25°) represent the values of the heat of dilution given in Col 5 of Table X. The first column of Table XII gives the concentration in mols of NaCl/1000 g. H₂O, the second the concentration in mols H₂O/mol NaCl, and the third the heat of solution per mol NaCl. The fourth column gives the heat absorbed when *M* mols of salt are dissolved in 1000 g. of water.

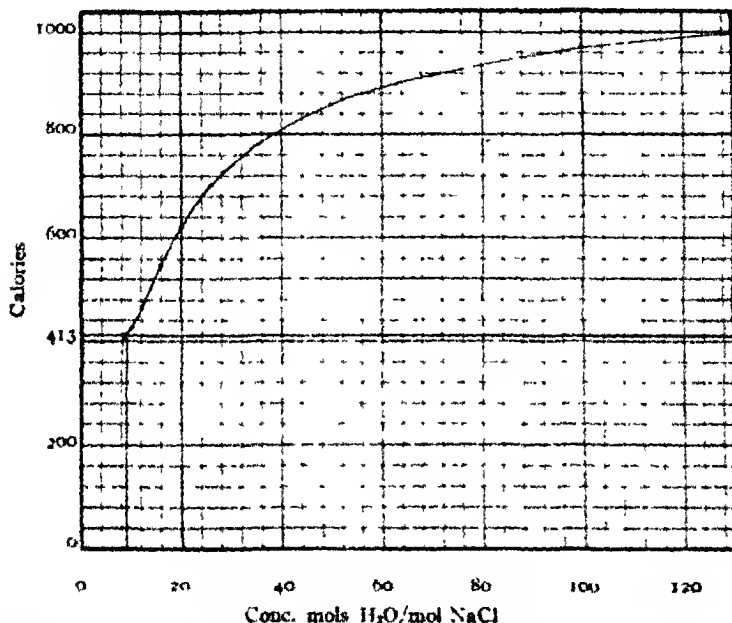


Fig. 9—Heat of solution of sodium chloride in aqueous sodium chloride solution.

Partial Molal Heat of Solution and the Partial Molal Heat Content of Sodium Chloride in its Aqueous Solution.—The values given in the last column of the preceding table were plotted against the concentration expressed in mols NaCl per 1000 g. H₂O, and values dh/dM , or the partial molal heat content of the sodium chloride in the solution, were obtained by reading off the tangents of the curve at the various concentrations given in the first column of Table XIII. The second column gives the partial molal heat content of sodium chloride. Thomsen found for the heat content of sodium chloride at room temperature, -97690 cal., while Berthelot found -97900 cal. We will use the value $\Delta h(\text{NaCl}(s)) = -97800$ cal. The values of $\Delta h(\text{NaCl}, x \text{ mols})$ are given in the last column of Table XIII.

TABLE XIII.—THE PARTIAL MOLAL HEAT CONTENT OF NaCl IN ITS SOLUTION AT 25°.

M.	$\bar{H} - \bar{H}(\text{NaCl})$	$\Delta \bar{H}(\text{NaCl} \pm M)$.
6.12	300	-97,500
5.55	268	-97,532
4.63	216	-97,584
3.47	232	-97,578
2.78	314	-97,486
2.13	433	-97,367
1.632	503	-97,297
1.110	636	-97,162
0.793	746	-97,054
0.555	855	-96,945
0.370	963	-96,835
0.278	1010	-96,790
0.0	1016	-96,781

The Functional Relation between the Values of the Partial Molal Heat Content of the Water and of the Sodium Chloride in the Solutions. —Having obtained the values of $\Delta \bar{H}$ or $\bar{H} - \bar{H}$ for both the solvent and the solute, we may now apply Equation 1 to these values. By the application of this equation we can make a careful scrutiny of the experimental results. It must be emphasized, however, that in applying the equation as has been done in this case, we have made use of not the individual values, but the average, which results in drawing a curve, more or less smooth, through these points.

In Table XIV the first column gives the concentration, the second the ratio of the mol fraction of solvent and solute, the third the rate of change of $\bar{H}(\text{H}_2\text{O})$ with the concentration determined by reading the tangents to the curve in Fig. 7, the fourth the rate of change of $\bar{H}(\text{NaCl})$ with the concentration as calculated by means of Equation 1, and the last the value of this quantity as given by the tangents of the $\bar{H}(\text{NaCl})$ curve in Fig. 7.

TABLE XIV.—THE CHANGE OF THE PARTIAL MOLAL HEAT CONTENT OF THE CONSTITUENTS WITH THE CONCENTRATION

M	$\frac{n_1}{n_2}$	$\frac{d\bar{H}(\text{H}_2\text{O})}{dM}$	$\frac{d\bar{H}(\text{NaCl})}{dM}$ (calculated)	$\frac{d\bar{H}(\text{NaCl})}{dM}$ Observed
6.12	9.04	-8.6	78	56
5.55	10.0	-8.4	84	60
4.63	12.0	-3.5	42	50
3.47	16.0	4.6	-74	36
2.78	20.0	6.7	-131	-160
2.13	26.0	7.8	-203	-175
1.632	34.0	6.9	-235	-200
1.110	50.0	6.0	-300	-305
0.793	70.0	6.0	-420	-430
0.555	100.0	4.6	-460	-360
0.370	150.0	2.5	-375	-475
0.270	200.0	1.4	-280	-230
0.0	∞	0	0	0

An inspection of the curves in Fig. 7 will show that if the slope of one of the curves is negative, that of the other is positive. The agreement of the calculated and observed values of the rate of change of $\bar{h}(\text{NaCl})$ with concentration is probably within the limits of error of plotting. In a sense the two sets of experimental data used in calculating $\bar{h}(\text{H}_2\text{O})$ and $\bar{h}(\text{NaCl})$ are not entirely independent, for we integrated the values of $\bar{h}(\text{H}_2\text{O})$ and thus obtained values which were used, together with some independent data, to establish the curve which was differentiated graphically to obtain $\bar{h}(\text{NaCl})$. Several conclusions as to the shape of the $\bar{h}(\text{H}_2\text{O})$ concentration curve (Fig. 7) are, however, on the basis of Table XIV, probably justifiable. While the points upon this curve are the results of direct measurements, these experiments are exceedingly difficult and tedious, and despite the observance of very considerable precaution a sort of systematic error is likely to appear and not be found out for some time. The value of $\bar{h}(\text{H}_2\text{O})$, 0.55 cal., at approximately 0.4 *M* is probably too high. The slight bulge upward in the curve at approximately 3 *M*, which from the experiments appears to have experimental significance, probably should not exist. The shape near the maximum is rather uncertain, and the values interpolated from a curve in a region of this sort will depend upon the function of the concentration and upon the scale which has been chosen for the plot. In this connection the two curves shown in Figs. 7 and 8 are interesting.

We have not been able to compare our results with those of other investigators. Thomsen's experiments were made at about 18°. Brönsted's experiments were probably at about the same temperature. The temperature coefficient for these reactions is rather large and has not been determined with sufficient accuracy to make the results comparable. Thomsen made one or two experiments on the heat of dilution of sodium chloride at 25°, which agree roughly with ours. Rumelin, who added small amounts of water to concentrated sodium chloride solutions, made a few measurements at various temperatures near 14°.

It is hoped to continue the present investigation to include potassium chloride, hydrogen chloride and other simple substances, as well as substances which do not dissociate and those which dissociate into polyvalent ions. The investigation would include not only the determination of the partial molal heat content over the entire range of solubility, but also the partial molal heat capacities, the partial molal free energies, and a comparison of the free energy of dilution, as determined from freezing point and thermal measurements, with those obtained by means of e. m. f. measurements.

BERKELEY, CAL.

G. FUSEYA.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 121.]

THE SOLUBILITY OF MERCURIC OXIDE IN SODIUM HYDROXIDE SOLUTIONS.

By G. FUSEYA.

Received November 29, 1919.

CONTENTS: 1. Introduction. 2. Purification of the Materials. 3. The Experimental Method 4. The Solubility Values. 5. Discussion of the Results

1. Introduction.

The erratic behavior of some mercuric oxide electrodes towards solutions of sodium hydroxide led to an investigation of the possibility of a compound resulting from the interaction of the oxide and the sodium hydroxide. The method adopted for studying the existence of such a compound is the determination of the solubility of mercuric oxide in sodium hydroxide solutions of various concentrations.

I desire to express my thanks to Profs. A. A. Noyes and D. A. MacInnes for their valuable suggestions and assistance.

2. Purification of the Materials.

To prepare the mercuric oxide, mercury purified by 3 distillations *in vacuo* was dissolved in nitric acid, and the solution was evaporated to dryness. The resulting mercuric nitrate was decomposed by heating it in a casserole over a gas burner. This yielded a deep red crystalline oxide. To remove the very finely divided material the oxide was repeatedly shaken with water which was poured off before all the particles had settled.

The sodium hydroxide solutions, which were carbonate free, were made by the electrolytic decomposition of sodium amalgam. The amalgam was prepared by the electrolysis of c. p. sodium hydroxide. The solutions were made from conductivity water collected from the special still in this laboratory.

3. The Experimental Method.

The solubility determinations were carried out by sealing the sodium hydroxide solutions, together with an excess of the red oxide of mercury, in glass tubes of about 150 cc. capacity. One-half of the tubes, containing the alkali at a given concentration, were placed immediately in a rotating device in a thermostat which was kept at $25^{\circ} \pm 0.01^{\circ}$. In order to approach the equilibrium also from the supersaturated side, the other half of the tubes were first agitated for 4 days in a thermostat at 40° . These tubes were then transferred to the thermostat at 25° . All of the tubes were rotated for 4 days at the latter temperature; after which they remained in the thermostat for 24 hours in order to allow the greater part of the oxide to settle. From each of the tubes 100 cc. of the solution was withdrawn through a filter of cotton fiber; and, after

acidifying with hydrochloric acid the mercury present was precipitated with hydrogen sulfide. The sulfide precipitate was then transferred to a perforated crucible, dried at 110° , and weighed.

4. The Solubility Values.

The results of the experiments are presented in the following table. The headings are for the most part self-explanatory. The solubility values within parentheses were omitted in taking the mean. Those marked by an asterisk were obtained with 200 cc. of solution taken from two tubes. The significance of the equilibrium constants given in the last column will be described in the next section.

TABLE I.—THE SOLUBILITY OF MERCURIC OXIDE IN SODIUM HYDROXIDE SOLUTIONS

Mols. per liter of solution		Milligrams of HgS from 100 cc. of solution		Mean	Millimols HgO per liter	Equilibrium constant
NaOH	OH ⁻ .	From under-saturation	From super-saturation			
2.09	1.253	7.30	7.30	7.20	30.9	0.0051
1.0758	0.7660	6.50 (6.80)	6.55 6.50	6.52	28.3	0.0050
0.502	0.4257	6.20*	6.25* 6.05	6.17	26.6	0.0049
0.0955	0.0863	5.00 5.90 5.75*	5.55* 5.75*	5.79	24.9	0.0047
0.0503	0.0465	5.75*		5.75	24.7	
0.0096	0.0091	5.60*	5.85 5.75	5.73	24.6	
0.0000	0.0000	5.50 (5.90) 5.30 5.40*	5.42 5.45*	5.43	23.4

5. Discussion of the Results.

In Fig. 1 the lower graph is a plot of the concentrations of mercuric oxide as ordinates against the sodium hydroxide concentrations as abscissas; and the upper graph is a plot of the concentrations of the mercuric oxide against concentrations of hydroxide ion, obtained by multiplying the alkali concentrations by the corresponding equivalent conductance ratios, as given by data from Noyes and Falk.¹

It will be observed that the value for the solubility in pure water does not fit on either of the graphs. This sudden change of behavior of the oxide, when passing from a neutral solution to one slightly alkaline, can hardly be due to an experimental error; for Schick² and Hulett³ have found values of the solubility in water that agree closely with that (23.4)

¹ THIS JOURNAL, 34, 454 (1912).

² Z. physik. Chem., 42, 155 (1903)

³ Ibid., 37, 401 (1901).

given in Table I; their determinations leading to 23.8 and 23.0 millimols per liter, respectively. The most probable explanation of this sudden change of solubility is that the oxide undergoes a dispersion into much finer particles when it is introduced into an alkaline solution. Red and yellow forms of the oxide are known; but it is generally considered

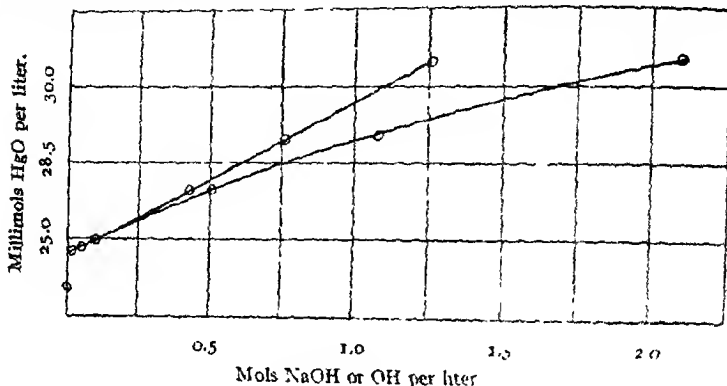


Fig. 1.

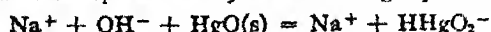
that the only difference between them is that the latter is in a finer state of division. Cohen¹ has found that there is a difference of 0.685 millivolt when the two forms of the oxide are made into electrodes of the form $\text{Hg} + \text{HgO}, \text{KOH}$. This is to be expected since finely divided substances have greater solubilities than coarsely crystalline ones. On the other hand, Schick² found that the two oxides have, within the experimental error, the same solubility in water, but it seems probable that in the prolonged agitation with water during his investigation the yellow substance was transformed into the red one. In this laboratory the reverse of this process, the change from red to yellow, has been observed to take place when the oxide is shaken with a solution of an alkali for a few hours. Evidently the disintegration of the red substance occurs even in very dilute alkali solution. This being the case, the finely divided form might be expected to be more soluble than the red variety. And, in fact, the extension of the lines of Fig. 1 to the zero ordinate doubtless gives the solubility in pure water of the yellow substance that was present in these experiments. The value of this solubility is 24.5 millimols per liter.

The steady increase of the solubility of mercuric oxide as the concentration of sodium hydroxide is increased indicates that the hydrated oxide functions as a very weak acid. Since the increase in solubility is pro-

¹ *Z. physik. Chem.* 34, 69 (1900).

² *Loc. cit.*

portional to the first power of the hydroxide ion concentration, the equilibrium is doubtless represented by the following equation:



The equilibrium constant K of this reaction is evidently given by the expression $K = (\text{HHgO}_2^-)/(\text{OH}^-)$. Now the concentration of the anion HHgO_2^- at each concentration of sodium hydroxide is equal to the observed solubility s of mercuric oxide in the solution less its solubility s_0 in water, multiplied by the degree of ionization γ' of the sodium mercurate; that is $(\text{HHgO}_2^-) = (s - s_0)\gamma'$. Owing to the slight solubility of the mercuric oxide the concentration of the sodium hydroxide is not appreciably affected by its presence, and the hydroxyl ion concentration becomes $c\gamma$, where c is the total concentration of the sodium hydroxide and γ its ionization. The expression for the equilibrium constant then becomes $K = (s - s_0)\gamma'/c\gamma$.

The values of this equilibrium constant are given in the last column of Table I. They were computed under the assumption that the ionizations of the sodium mercurate and sodium hydroxide in the presence of each other are equal (that $\gamma' = \gamma$), and by using for the solubility in water s_0 the extrapolated value (0.0245) instead of the observed one.

An estimate of the ionization constant of the mercuric acid $\text{H}^+ \text{HHgO}_2^-$ may also be made. If the acid is represented by HA , the ionization-constant $K_A = (\text{H}^+)(\text{A}^-)/(\text{HA})$. Substituting for (H^+) its value from $K_w = (\text{H}^+)(\text{OH}^-)$ and for the ratio $(\text{A}^-)/(\text{OH}^-)$ the constant K just described, we obtain $K_A = K_w K/(\text{HA})$. For the value of (HA) the (extrapolated) solubility of mercuric oxide may be used. This expression involves the additional equilibrium, $\text{HgO} + \text{H}_2\text{O} = \text{H}_2\text{HgO}_2$; but the equilibrium constant of this hydration reaction is included in the ionization constant, as in the analogous cases of the ionization constants of ammonium hydroxide and carbonic acids.

By substituting in this equation for K_w the value¹ 0.81×10^{-14} , for K the value 5.0×10^{-2} (the mean of the first 3 values given in Table I, and for (HA) the value 24.5×10^{-3} , we find for the ionization constant of the first hydrogen of mercuric acid (H_2HgO_2) the value 1.7×10^{-13} .

CAMBRIDGE, MASS.

¹ Lewis and Randall, *THIS JOURNAL*, 36, 1979 (1914).

CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA I

THE VELOCITY OF ADSORPTION OF CHLOROPICRIN AND CARBON TETRACHLORIDE BY CHARCOAL.¹

BY HERBERT S. HARNED.

Received December 6, 1919

This investigation has been pursued with the purpose, first, of obtaining reproducible results in the measurements of the velocity of adsorption of gases on a relatively gas-free solid surface, and, second, of determining the effect of the presence of a foreign gas on this velocity of adsorption. The method of weighing the gas adsorbed at selected time intervals of exposure of the surface to the gas has been employed throughout. The advantage of this method lies in its directness and simplicity, but is limited to the cases where relatively large weights of gases are adsorbed. For this reason, the present investigation has been confined to the study of two gases of relatively high molecular weight on a solid which for unit weight, affords an exceedingly large surface.

Apparatus and Method of Measurement.

The apparatus employed was designed to accomplish 3 operations: (1) To purify the liquid used as the source of gas by 2 distillations in vacuum, accompanied by a special operation which assured the efficient removal of all gases dissolved in the liquid, (2) to permit the heating of the charcoal to temperatures up to 1100° in a vacuum produced by mercury vapor pumps; (3) to permit exposures of the charcoals for definite and selected time intervals to the constant pressure of the gas.

Fig. 1 shows a sketch of the essential part of the apparatus. The tubes A, B, and C were evacuated, and a dried sample of the liquid of high purity was sucked in through a capillary tube at *b*, which was then sealed off. The tubes A, B, C were again evacuated and the liquid was slowly distilled from A to B by immersing B in liquid ammonia contained in a Dewar bulb or in a suitable salt-ice mixture. The stopcock 1 was kept closed during this operation. The tube B contains a device, *a*, which serves both as a stirrer and a means of indicating with great delicacy whether or not the liquid is air-free.² The bottom part of *a* is a small inverted cup, the center portion is a glass tube, sealed on to the cup, which contains an iron bar, indicated by the cross hatching. The

¹ A part of the work here presented was started at the suggestion of Major Frederick G. Keyes, Director of the Chemical Warfare Service Laboratory in Paris. Initially it was merely intended to determine by direct experiment the influence of air and moisture already adsorbed by charcoal on the rate of adsorption of chloropicrin. The study has been continued and extended at the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

² Young, *Phil. Mag.*, 20, 793 (1910), see also Keyes and Felsing, *This Journal*, 41, 604 (1919).

upper part is a closed glass tube slightly less in diameter than the inside diameter of B. By means of a solenoid around the tube B, *a* can be raised and lowered at will. When the liquid is free from dissolved gas vapor entrapped in the inverted cup will quickly and completely condense under the hydrostatic pressure when the cup is lowered. A very small quantity of gas dissolved in the liquid will prevent this. By repeatedly stirring the liquid in B under suction it was completely freed from dissolved air. C was then heated to 250° in a vacuum in order to remove any gases adsorbed on the glass wool contained in it until the pressure was reduced to 10^{-6} mm. of mercury, cooled to room temperature and immersed

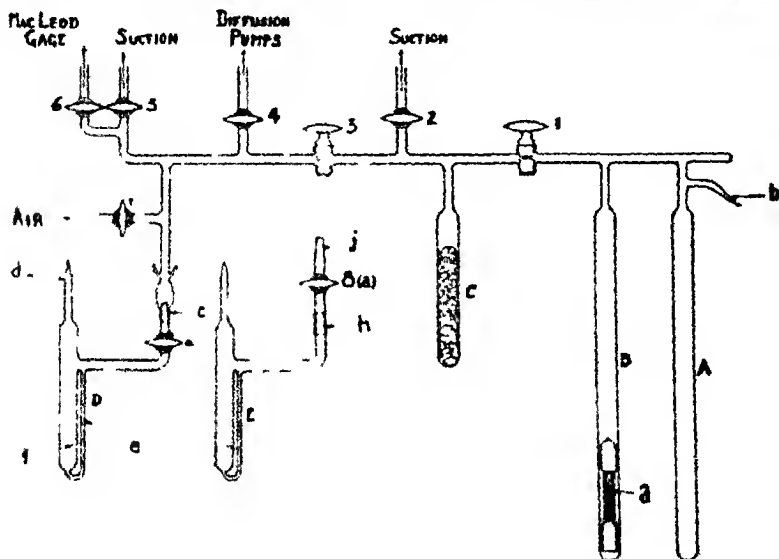


Fig 1

in an ice and salt mixture or liquid ammonia. Stopcocks 2 and 3 were closed, 1 was opened and a fraction of the liquid in B was distilled into C after which the stopcock 1 was again closed. The distillation was carried on slowly so that no liquid came into contact with the grease used to lubricate the stopcocks. The tubes containing the liquid were always maintained below room temperature so that only vapor could come in contact with the grease. By exercising sufficient care, it was found that a properly lubricated stopcock could be used for at least one month without further attention. The glass wool was put in C in order to afford a large liquid surface available for evaporation.

Two types of weighing tubes containing the charcoal were employed, one made of Pyrex glass, the other of quartz, shown in Fig. 1 by D and E, res-

spectively. D is all Pyrex glass ground into soft glass at *c*. E is of quartz, ground into Pyrex at *h*, which in turn is ground into soft glass at *j*. 8 and 8(a) are Pyrex stopcocks. The inside diameter of these cocks at the narrowest point was 2 mm. The charcoal was introduced through *d* or through *h*, respectively, and rested on the diaphragms *f*. *d* was sealed off. The tube *e* serves the purpose of introducing the gas from both sides of the charcoal. The weighing tubes could be connected to suction (geared oil vacuum pump), to the mercury-vapor pump, to a MacLeod gage or to air, by operating Cocks 4, 5, 6, 7, and 8. The mercury-vapor pumps were made of Pyrex glass and were similar in design to those described by Kraus¹. For a time an oil pump which produced an average vacuum of 0.001 mm. of mercury was connected to a mercury-vapor pump, later, a Cenco-Nelson pump averaging 0.05 mm. of mercury was connected to two mercury vapor pumps of the proper design in series. Both these systems would give a pressure of 0.01 bar. The tubes D and E were weighed against a suitable counterpoise. They were heated by a small electric resistance furnace. Dewar tubes containing suitable liquids or ice mixtures were used to maintain D or E and C at the desired constant temperatures.

After the preliminary purification of the liquid, the tube C was immersed in a thermostat and maintained at constant temperature. This will give a constant pressure of vapor from the liquid. The charcoal was then heated in a vacuum for some hours and then Stopcock 8 or 8(a) was closed. The apparatus was then evacuated with the cocks 3, 5, 7 closed until a vacuum of 10^{-6} mm. was reached. Stopcocks 4 and 6 were closed and 3 was opened, then 8 was opened for a definite time interval. The velocity of diffusion of a gas into a high vacuum is very high, approaching the mean average velocity of molecules; and, hence, practically instantaneous contact of the gas with the charcoal was obtained. After the exposure, the cocks 4, 8, 6 and 3 were closed, 7 was opened and the weighing Tube D or E was withdrawn and weighed, after which the same operation was repeated. Correction was made for the volume of the weighing tube (approximately 10 cc.). The principal source of error in these measurements results from the difficulty and time taken to turn the cocks 8 or 8(a). With practice, this operation can be carried out successfully to within ± 0.1 of a second. When low pressures of gas are employed, the adsorption takes place so slowly that this error becomes negligible.

Results.²

I. Chloropicrin Adsorption.

A. The first series of results was obtained by using a wood charcoal

¹ THIS JOURNAL, 39, 2183 (1917)

² Series A and C and No. 4 Series B were obtained in Paris, all other results in Philadelphia.

(French canister charcoal of 14 to 16 mesh) which contained 6.0% non-volatile material. The Pyrex glass weighing tube D (Fig. 1) was used.

(1) Wt. of charcoal equalled 0.843 g. Heated to 350° for 2 hours in a high vacuum, cooled and maintained at 20° ± 1°. The tube C (Fig. 1) containing chloropicrin was kept in ice water contained in a Dewar bulb. By keeping the liquid reservoir at a temperature lower than the charcoal, distillation was avoided. Vapor pressure of chloropicrin at 0° = 5.90 mm. of mercury.

(2) Same charcoal, same weight as in (1). No air or moisture was permitted to come into contact with the charcoal between measurements (1) and (2). Reheated to 350° for 2.5 hours in a high vacuum. Gain in weight of charcoal equalled 10 mg. Same temperature conditions during velocity measurements as in (1).

(3) Same charcoal. Reheated to 350° for 7 hours in a high vacuum. No foreign gas admitted. Gain in weight of charcoal equalled 1.5 mg. Same temperature conditions as in (1) and (2).

Table I contains the results of Series A.

TABLE I
Chloropicrin. $p = 5.90$ mm. t = Time of Exposure in Seconds K = Wt. of Gas adsorbed per g. of Charcoal in Time t

1		2		3	
t	K	t	K	t	K
1.6	0.0030	1.6	0.0056	2.2	0.0091
3.2	0.0070	2.8	0.0082	5.4	0.0221
5.7	0.0116	5.1	0.0159	8.6	0.0374
9.1	0.0241	7.4	0.0214	13.8	0.0568
14.4	0.0418	9.7	0.0305	24.3	0.0753
25.1	0.0636	15.0	0.0479	6600.0	0.1854
463.0	0.1578	25.4	0.0728		
...	..	503.0	0.1406		..

The t , K plots of these results are given in Fig. 2

B. Since there was an increase in weight of the charcoal with each successive determination, it was decided to use much higher temperatures in the further investigations, in order to drive off any chloropicrin remaining on the surface. To this end a transparent quartz weighing Tube E (Fig. 1) was employed. In the second place, since the non-volatile matter in the charcoal was so high, it was considerably reduced by a process of extraction.

(4) Another portion of the same sample of charcoal used in Series A was extracted in a Soxhlet extractor with constant boiling hydrochloric acid for 16 hours, then with water for 8 hours. It was finally heated in a muffle furnace for 15 minutes at 900°. The ash from two samples of this material was 1.0% and 1.3% respectively.

Wt. of charcoal used equalled to 0.5233 g. This was heated in a high vacuum to 700° for 2.5 hours. Charcoal at 20.0 ± 1°, chloropicrin at 0° during the velocity measurement.

(5) Another sample of charcoal extracted and ignited as in (4).

Wt. charcoal used equalled 0.5146 g. This was heated to 750° for 4 hours. Charcoal at 20°; chloropicrin at 0° during the measurement.

(6) Same charcoal as in (5). Reheated to 800° for 8 hours in a high vacuum. No foreign gas was permitted to come into contact with the charcoal between measurements.

HERBERT S. HARNED.

ments (5) and (6). Gain in weight of charcoal equalled 0.4 mg. Charcoal at 20° chloropicrin at 0° C.

(7) Same charcoal as in (6). Reheated to 800° for 2 hours in a high vacuum. Charcoal unexposed to foreign gases between measurements (6) and (7). Charcoal at 20°, chloropicrin at 0°

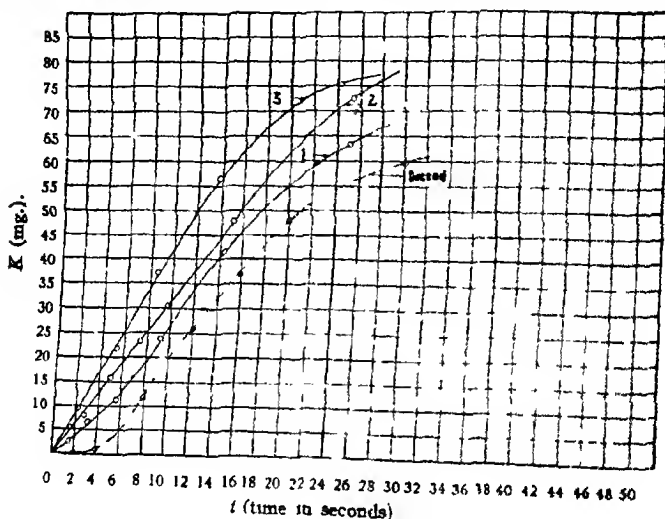


Fig. 2.

The results of Series B are given in Table II

TABLE II
Chloropicrin $p = 5.90$ mm

4		5		6		7	
t	K	t	K	t	K	t	K.
1.9	0.0138	10.0	0.0743	10.0	0.0901	10.0	0.0875
4.9	0.0340	21.0	0.1345	21.0	0.1520	21.0	0.1493
10.0	0.0671	32.0	0.1800	32.0	0.1963	32.0	0.1930
20.0	0.1284	44.0	0.2168	44.0	0.2340	44.0	0.2328
30.0	0.1666	57.0	0.2343	57.0	0.2556	57.0	0.2580
43.0	0.2300	80.0	0.2485	80.0	0.2820	80.0	0.2862
65.0	0.2560	137.0	0.2702	500.0	0.3083	
85.0	0.2695	20.0 (min)	0.3085			
125.0	0.2724					
1625.0	0.2972					

The K, t plots of these results are given in Fig. 3

In this series of measurements, the pressure of the chloropicrin was reduced by immersing the Tube C (Fig. 1) in liquid ammonia contained in a Dewar bulb. This reduced the gas pressure to a magnitude of approximately 0.61 mm of mercury of $1/10$ of the pressure employed in Series

A and B. This value for the vapor pressure of chloropicrin at -33.3° was obtained by extrapolation from the plot of the log of the vapor pressure against $1/T$, where T is the absolute temperature, which is a straight line for temperatures from $0-70^{\circ}$ and is, therefore provisional

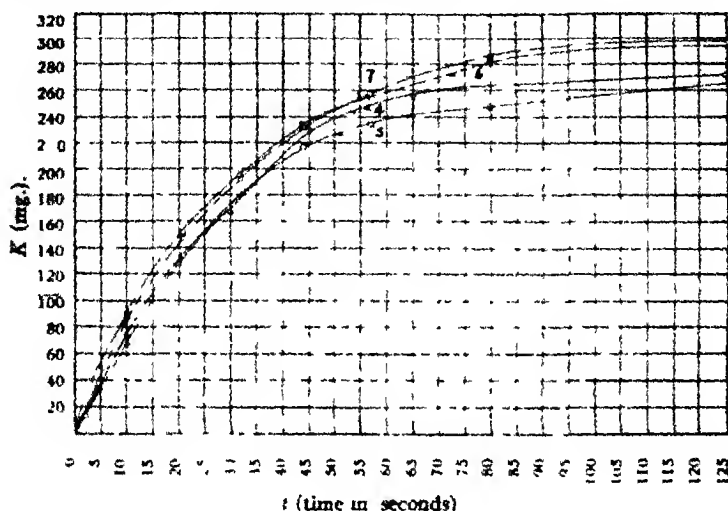


Fig 3

(8) The charcoal used in B (4), which has been extracted with hydrochloric acid, was covered with a hydrofluoric acid solution which was then evaporated to dryness. The charcoal was again extracted with hydrochloric acid and water, and finally heated to 900° for 15 minutes in a muffle furnace.

Wt. charcoal equalled 0.4294 g. Heated to 700° in a quartz weighing tube for 3 hours in a high vacuum. Chloropicrin at 33.3° , charcoal at 20° during the velocity measurement. Vapor pressure of chloropicrin equals 0.61 mm.

(9) Same sample of charcoal as in (8). Reheated to 700° in a high vacuum for 2 hours. No foreign gas was permitted to reach charcoal between (8) and (9). Charcoal at 20° , chloropicrin at 33.3° .

(10) Same charcoal as in (9). Reheated at 700° in high vacuum. No foreign gas admitted.

(11) Same charcoal as in (10). Heated in vacuum for 2 hours to 700° , then cooled to room temperature, then exposed to air at one atm. pressure for one minute, again heated for $1/2$ hour at 700° in a vacuum, and again exposed to air for one minute. This process was repeated 5 times. After this rinsing out process, the charcoal was cooled to room temperature, exposed to air for one minute, and then evacuated at room temperature for 30 minutes.

The results of Series C are contained in Table III.

These results are plotted in Fig. 4 along with a result obtained on the sample used in B (4) and denoted (c).

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TABLE III.
Chloropicrin. $p = 0.61$ Mm t is Given in Minutes.

8.		9.		10.		11.	
t .	K	t	K	t	K	t	K .
5.0	0.0002	5 0	0.0532	5 0	0.0571	5 0	0.0036
10 0	0.0012	10 0	0.0948	10 0	0.1034	10 0	0.0054
15 0	0.0037	15 0	0.1250	15 0	0.1385	15 0	0.0065
20.0	0.0051	20 0	0.1574	20 0	0.1683	25 0	0.0107
25 0	0.0077	30 0	0.1972	30 0	0.2089	40 0	0.0193
35 0	0.0149	40 0	0.2265	40 0	0.2329	60 0	0.0234
45 0	0.0237	50 0	0.2430	50 0	0.2351	80 0	0.0336
55 0	0.0347	70 0	0.2610	60 0	0.2378	100 0	0.0431
65 0	0.0470			90 0	0.2468	
85 0	0.0640			120 0	0.2541	
105.0	0.0771						..
135 0	0.0941						..

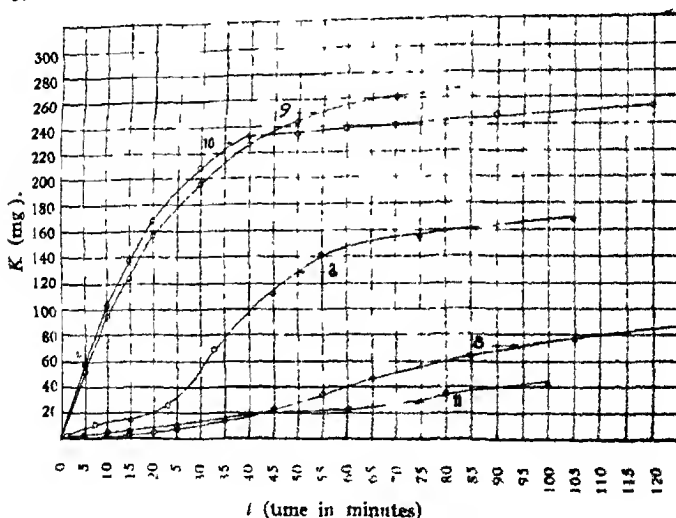


Fig. 4

II. Carbon Tetrachloride Adsorption.

In the following 3 series of measurements, the charcoal was exposed to the vapors of carbon tetrachloride maintained at a pressure of 32.8 mm. and 18.8 mm. of mercury.

D. (1) The charcoal used in this experiment was a sample of wood charcoal (French 14-16 mesh) which had been extracted with constant boiling hydrochloric acid, water and then heated to 900° for 15 minutes in a muffle furnace.

Wt. charcoal equalled 0.5447 g. Heated for 4 hours at 750° in a high vacuum. Charcoal at 20°, carbon tetrachloride at 0° during measurement. The vapor pressure of carbon tetrachloride at 0° is 32.8 mm. (Reference, "Landolt-Börnstein Tabellen.")

(2) Same charcoal as in D (1). Reheated in vacuum to 750° for 2.5 hours. There was a gain in weight of 0.0109 g. No foreign gases came in contact with charcoal between measurements D (1) and (2). Charcoal at 20° , carbon tetrachloride at 0° .

(3) Same charcoal as in D (2). Exhausted for $1/2$ hour at 30° . Then reheated in a high vacuum for 8 hours at 750° . Then again reheated for 1.5 hours to 800° in a high vacuum. The pressure over the charcoal with the pumps on the line equalled 4×10^{-4} mm. of mercury. There was a gain in weight of the charcoal of 0.0213 g. over D (2). Charcoal was maintained at 20° , carbon tetrachloride at 0° .

(4) Same charcoal as in D (3) was heated for 4 hours to 800° in a high vacuum. Exposed to air at atmospheric pressure for 10 minutes. Reheated for $1/2$ hour to 800° in a high vacuum. Cooled to 30° , exposed to air for one minute at atmospheric pressure. Gain in weight of charcoal over D (3) equalled 0.0037 g. Charcoal at 20° , carbon tetrachloride at 0° .

The results of Series D are given in Table IV.

TABLE IV.
Carbon Tetrachloride. $p = 32.8$ Mm. $t =$ Time of Exposure in Seconds.

1.		2.		3.		4.	
t	K	t	K	t	K	t	K
5 0	0.0187	5 0	0.0211	10 0	0.0280	20 0	0.0165
14.5	0.0341	15 0	0.0328	33 1	0.0860	50.0	0.0405
35.0	0.0499	35.0	0.0413	67 2	0.1607	80.0	0.0700
100.0	0.0717	100 0	0.0536	74 8	0.1962	110 0	0.0993
200 0	0.0814	180 0	0.0631	100 0	0.2011	150 0	0.1247
300.0	0.0881	420 0	0.0845	240 0	0.2024	230 0	0.1389
600 0	0.1029	1020 0	0.1123			470 0	0.1418
1200.0	0.1209	2420 0	0.1438				

The plots of these results are shown in Fig. 5.

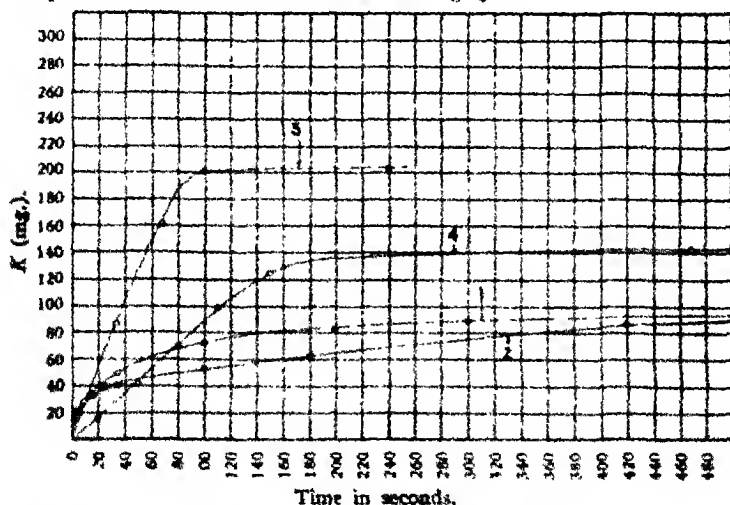


Fig. 5.

Another series of results with a fresh sample of charcoal was made under similar conditions to Series D but no greater

in the above table was obtained. Because of this discordancy and because of the fact that even after prolonged heating of the charcoal, constant weight was not obtained, it was decided to increase the preliminary heating of the charcoal to above 1000° .

E. (5) A fresh sample of charcoal, which had been extracted and treated in an identical manner as that employed in Series D was used

Non-volatile matter equalled 0.9%. Heated in a high vacuum to $1040-1060^{\circ}$ for 6.5 hours. Pressure in the system above the charcoal was finally reduced to 5×10^{-4} mm of mercury with the pumps on. Wt charcoal equalled 0.5391 g. Charcoal at 20° , carbon tetrachloride at 0° .

(6) Same charcoal as in E (5). Reheated to $1060-1080^{\circ}$ for 16 hours. The pressure above the charcoal was reduced to 8×10^{-4} mm with the pumps on. Gain in weight of charcoal equalled 0.0153 g or 28 mg per g of charcoal. Charcoal at 20° , carbon tetrachloride at 0° .

(7) Same charcoal as in E (6). Reheated to 1100° for 4 hours. Pressure above charcoal was reduced to 5×10^{-3} mm. Gain in weight of charcoal equalled 0.0100 g or 19 mg per g of charcoal. Charcoal at 20° , carbon tetrachloride at 0° .

The results of Series E are given in Table V.

TABLE V
Carbon Tetrachloride $\rho = 32.8 \text{ Mm}$ t — Time of Exposure in Seconds

t	Δ	t	Δ	t	Δ
10.0	0.0966	5.0	0.0872	5.0	0.0805
21.0	0.1383	10.0	0.1413	10.0	0.1284
43.0	0.1704	21.0	0.1855	21.0	0.1637
78.0	0.1949	42.0	0.2045	40.0	0.1826
136.0	0.2135	60.0	0.2060	80.0	0.1872
235.0	0.2239	250.0	0.2075	100.0	0.1878
500.0	0.2337	1000.0	0.2085		

The plots of these results are shown in Fig. 6.

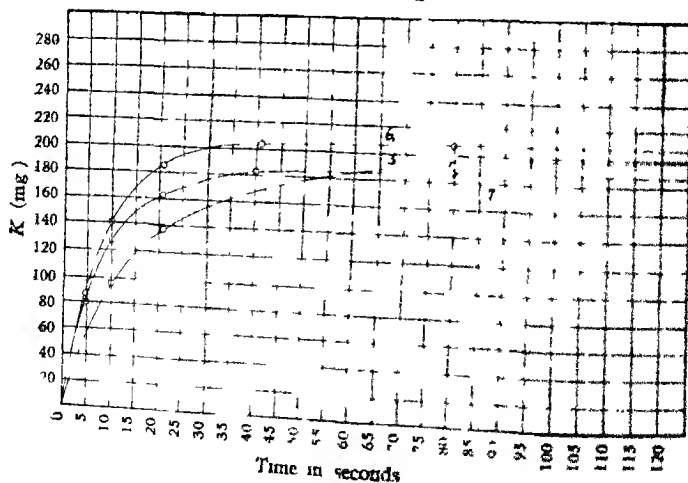


Fig. 6

F. In this series of results the gas pressure was reduced to 18.8 mm. by immersing the tube containing carbon tetrachloride in a salt-ice mixture contained in a Dewar bulb.

(8) Fresh sample of charcoal similarly treated to that used in E. Heated to 1060–1080° for 7 hours in a high vacuum. Cooled to room temperature in vacuum, then exposed to carbon tetrachloride (32.8 mm) for 2 minutes. Reheated for 6 hours to 1060–1080° in high vacuum. Charcoal at 20°, carbon tetrachloride at –10°.

(9) Same samples of charcoal as in F (8). Reheated to 1080–1100° for 3.5 hours in high vacuum. Gain in weight of charcoal equalled 14 mg per g charcoal. Charcoal at 20°, carbon tetrachloride at –10°.

The results of Series F are given in Table VI.

TABLE VI
Carbon Tetrachloride $p = 18.8$ Mm

8		9	
t	K	t	K
5.0	0.0583	5.0	0.0495
10.0	0.0941	10.0	0.0893
21.0	0.1460	21.0	0.1400
33.0	0.1782	33.0	0.1683
47.0	0.1915	48.0	0.1799
64.0	0.1963	66.0	0.1831
90.0	0.1975	92.0	0.1858
130.0	0.1980	120.0	0.1887
240.0	0.1998	240.0	0.1890

The plots of the results of Series F are shown in Fig. 7.

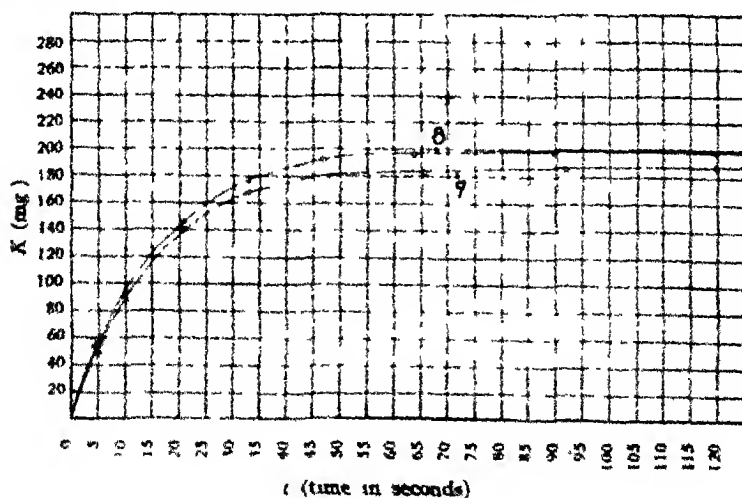


Fig. 7.

Discussion of Results.

The Initial Lag.—From measurements of the velocity of adsorption of various canister charcoals containing air, moisture, oxides of carbon and other gases, by passing a war-gas and air mixture over them, Keyes and Finklestein (A E F reports) found that the plot of $\log K$ against $1/t$ was a straight line, where K is the amount of war-gas in grams per g. of charcoal adsorbed in a time, t . Analytically, this expression becomes

$$K = Ae^{-B/t} \text{ or } \log K = \log A - B/t \quad (1)$$

where A and B are constants. A is the number of g. adsorbed per g. of charcoal when t is infinity, or the capacity constant, B is the rate constant. By differentiating (1), the equation,

$$\frac{dK}{dt} = \frac{AB}{t^2}$$

for the rate of adsorption is obtained. This equation has one interesting peculiarity. At first, the rate is slow, then it increases to a maximum, and finally decreases until equilibrium is reached. When $t = B/2$, dK/dt is a maximum.

A K, t plot using Equation 1 is shown by the dotted line in Fig. 2 where $A = 120$ (mg.), $B = 7$, t is in seconds and K in mg. This equation is purely empirical, and furthermore, the lag predicted by it had not been proved or disproved by direct experiment prior to the present work because the experimental method used by Keyes and Finklestein did not permit measurements to be made for small enough values of t .

A lag somewhat similar to this has been realized experimentally many times in this investigation. Curves A-1, A-2, A-3, C-8, C-11, and C-9, and D-8 are good examples, but do not, however, fit the above equation. It should be observed, however, that in the measurements here presented the charcoal has been probably deprived of a considerable portion of its adsorbed air by a preliminary heating in high vacuum and the charcoal surface probably uncovered considerably, whereas in the Keyes and Finklestein work charcoals completely saturated with air or air and moisture were employed. The behavior in both cases was thought to be due to the presence of foreign gases on the charcoal at the beginning and throughout the experiment, a considerable time delay being caused during their displacement.

2. The Effects of Foreign Gases.—The method of heating the charcoal to as high a temperature as was permissible in the apparatus employed in a high vacuum was well calculated to remove most of the foreign gases and eliminate this lag. There is much evidence, *e. g.*, as here presented and also by other investigators, that simply heating charcoal up to 1200° in a vacuum will not suffice to produce an absolutely gas-free

surface. For example, Chaney¹ reports that a hydrocarbon resembling anthracene, the boiling point of which is 360° , has been isolated from a cedar charcoal which had been previously calcined to 850° . However, relatively free surfaces may be obtained this way. In no case yet observed were anything like reproducible velocity results obtained until the charcoal had been heated to over 700° in a vacuum, cooled in a vacuum, exposed to the gas until considerable quantities were adsorbed, and then again reheated to above 700° in a high vacuum. This process of "washing out" the charcoal with the gas whose adsorption velocity was being measured seemed to be necessary under the temperature conditions employed before reproducibility could be obtained. The presence on the surface of molecules of the gas whose velocity of adsorption is being determined, and this gas alone, will not affect the form of the plots. In order to bring out more clearly the significance of the adsorption behavior, it will be necessary to consider each of the series of results obtained.

Series A, Fig. 2 — These curves show the successive effect of "washing out" and heating in vacuum to 350° . Curve 1 has a decided lag, Curve 2 less, Curve 3 still less but reaching a maximum rate only after the expiration of 7 minutes. These curves lie somewhere between those obtained by the equation of Keyes and Finklestein for completely air saturated charcoal of the same kind and the curves which will be obtained after a more effective removal of foreign gases from the surfaces. No regularity in the experimental results was observed at values of t above 30 seconds (results not tabulated), and even after exposures of 110 minutes, the full capacity of the charcoal was by no means obtained. These curves are valuable for illustrating the gradual elimination of the lag by successive heating and washing out of foreign molecules.

Series B, Fig. 3. — In these results, the more effective cleansing of the surface at higher temperatures (700° as compared to 350°) is to be observed. Curve 4 (obtained in Paris) was the first obtained in which the initial lag was entirely eliminated. The maximum rate occurs at the very beginning of the process. Curves 5, 6 and 7 give the history of a charcoal which was reheated and "washed out" twice. Curves 6 and 7 are regarded as reproducible because they are easily rectified by a simple equation. In Fig. 8, $\log A/A - K$ is plotted against t , where K the amount adsorbed in time t and A is the amount adsorbed when t is infinite or the capacity factor. The plot is a straight line, B-6 and -7.

In addition, no faster adsorption was caused by further repetition of the above successive heating and pumping treatment. Curve 5 represents a slower adsorption, because it has only been heated and not "washed out" with chloropicrin. It is very interesting at this juncture to compare the rapidity with which the total capacity is reached in Experiments B-4,

¹ *Trans. Am. Electrochem. Soc.*, Paper 13, Sept. 26, 1919.

6, 7 and those described in Series A. In Series B, the charcoal was filled in practically 100 seconds, in Series A3 only 0.1854 g. was adsorbed in 6600 seconds, corresponding to only 60% of the capacity in $1/100$ of the time.

Series C, Fig. 4.—In these measurements, a pressure of 0.61 mm. of chloropicrin was employed. This pressure, 10 times less than that employed above, was used to magnify any effect due to foreign gases on the surface. Curve *a* has been introduced solely for the purpose of showing the initial lag. It is best to observe Plots 8, 9, 10 and 11 in order, which give the history of one sample of charcoal. Curve 8 is extremely slow; there is no doubt from this of the existence of the initial lag. The maximum rate occurs in about 60 minutes from the start. When this charcoal was rinsed out with chloropicrin by reheating in a high vacuum, Curve 9 was obtained. In the first 5 minutes, the charcoal had taken up 250 times the quantity of gas; in the first 10 minutes, 90 times the quantity and so forth. This shows the great efficiency of the "washing out" process.¹ Furthermore, Plot 9 is rectified by the same equation which rectified Series B, 6 and 7. The plots of $\log A/A - K$ against t are given in Fig. 9. The same is true of Curve 10 which varies only slightly from 9; with the exception of a sharp break occurring when t equals 40, which was probably caused by a slight inrush of air into the apparatus. As further proof that these abnormal effects are due to the presence of foreign gases, the charcoal used in Expt. 10 was rinsed out as described and some air was allowed to remain on the surface. The original slow process was nearly reproduced. The amount of foreign gases necessary to cause this remarkable change cannot be given. The charcoal was 0.0002 g. heavier in Expt. 11 than in 10. However, repeated heating in the presence of air must have caused the burning off of some of the charcoal.² Further investigations of these phenomena will be made.

At this point it may be said that whenever the curves can be closely reproduced as with B-6 and -7, C-9 and -10, they all conform to the same equation. All other curves which do not fit the form of this equation vary in a most erratic manner as illustrated by Curves *a*, 8 and 11 (Fig. 4) and D-1, -2, -3 and -4 (Fig. 5).

Series D, Fig. 5.—These results were obtained with carbon tetrachloride at a pressure of 32.8 mm. of mercury. Curve 1 shows results obtained after heating the charcoal to 750° in a vacuum. Curve 2, after a first reheating to 750° and rinsing with carbon tetrachloride; and Curve 3

¹ To offer a crude analogy, it is similar to soaking up gasoline with a sponge which is already covered with a film of water. Practically no gasoline will be taken up until the sponge is washed out a number of times with gasoline.

² Langmuir, *THIS JOURNAL*, 40, 1400 (1918), has observed a similar behavior in studying the velocity of the reaction between oxygen and carbon monoxide on platinum foil. In the latter instance erratic slow and fast reactions were observable when no foreign gas was present in sufficient quantities to form a film one molecule thick.

after a second reheating to 750° in a vacuum and a second rinsing. The effects of the presence of foreign gases on the surface were very noticeable. Although Curve 3 shows a large increase in velocity over 1 and 2, it does not conform to the form of curve found for B-6 and -7, C-9 and -10. The experiments in 4 were carried out in the presence of air and exhibit a lag. Another series of 5 results, not included in the data, was carried out in the same manner, and the results were as discordant and as unpredictable as the above. Even after a continued exhaustion at 750° , a considerable gain in weight of charcoal was observed.

Series E, Fig. 6.—The exhaustion of the charcoal in the 3 experiments in this series was carried out at from 1050 – 1100° . This made a notable difference in reaction velocity. Curve 5 was obtained after the first heating, 6 after reheating and rinsing out with the gas, and 7 after a second reheating and rinsing out process. Curves 6 and 7 are identical in form and are rectified by the same equations as B-6 and -7, C-9 and -10. The plots of $\log A/A - K$ against t are given in Fig. 8. There is a difference, however, in final capacities between E-5, -6 and -7 which corresponds closely to the gain in weight of the charcoal between the measurements. Even a continuous exhaustion for 16 hours at 1060 – 1100° failed to reduce the weight of the charcoal to the original weight. In fact, between Expts. 5 and 6, the charcoal had gained 28 mg. per g. The decrease in final capacity between Expts. 5 and 6 was 25 mg. per g. Again, the gain in weight of charcoal between Expts. 6 and 7 was 19 mg. per g. The decrease in final capacity was 21 mg. per g. This is proof that a considerable quantity of carbon tetrachloride is held by the surface at temperatures from 1060 to 1100° . Others have reported that hydrocarbons are held by charcoal at these temperatures.¹

Series F, Fig. 7.—What has been said of Expts. E-6 and -7 may be said of F-8 and -9. The only difference in behavior is due to the fact that the gas pressure has been lowered from 32.8 mm. to 18.8 mm. The plots of $\log A/A - K$ against t are also given in Fig. 8.

General Considerations.

Langmuir² has developed a general theory of adsorption of gases on solids. From consideration of the unsymmetrical arrangement of the atoms of the surface of a solid, it is assumed that they are "unsaturated chemically and thus are surrounded by an intense field of force." Further, "when gas molecules impinge against any solid or liquid surface they do not, in general, rebound elastically, but condense on the surface, being held there by the field of force (residual valence) of the surface atoms. These molecules may subsequently evaporate from the surface. The length of time that elapses between the condensation of a molecule and its subse-

¹ Chaney, *loc. cit.*

² THIS JOURNAL, 40, 1361 (1918).

net evaporation depends on the intensity of the surface forces. Adsorption is the direct result of this time lag. If the surface forces are relatively intense, evaporation will take place at only a negligible rate, so that the surface of the solid becomes completely covered with a layer of molecules. In cases of true adsorption this layer will usually be not more than one molecule deep, for as soon as the surface becomes covered by a single layer, the surface forces become chemically saturated. Where, on the other hand, the surface forces are weak the evaporation may occur so soon after condensation that only a small fraction of the surface becomes coated with a single layer of adsorbed molecules. In agreement with the chemical nature of the surface forces, the range of these forces has been found to be extremely small, of the order of 10^{-8} cm. That is, the effective range of the forces is less than the diameter of a molecule.

Case 1.—In the present investigation the pressure of the gases has been kept sufficiently low to eliminate any "capillary effects," so that the phenomena are cases of true adsorption. In accordance with the above scheme, let it be assumed that we have to do with a film one molecule thick. Let it also be assumed that the ratio of the number of molecules condensing on unit surface in unit time to the number evaporating from the surface is a constant throughout the process. Furthermore, let it be assumed that all molecules of the gas which impinge on the layer of molecules already on the surface, rebound and do not condense. With such conditions, the velocity will then be proportional to the bare surface, which, expressed in the quantities measured, becomes

$$\frac{dK}{dt} = m(A - K), \text{ or } m = \frac{1}{t} \ln \frac{A}{A - K} \quad (3)$$

where A is the total weight capacity per g. of charcoal, K is the weight absorbed per g. of charcoal in time t , and m is a constant. Langmuir's Equation¹ 15 which takes into consideration the factors of surface, condensation and evaporation involved is

$$\frac{N}{N_0} v_1 \left(1 + \frac{\alpha}{v_1} \mu \right) = \frac{1}{t} \ln \frac{\theta_1}{\theta_1 - \theta'}$$

where N_0 represents the number of the elementary spaces per sq. cm. of surface, N is Avogadro's number, α the fraction of the number of molecules which condense on the surface, μ is the number of gram molecules of gas striking each sq. cm. surface per second, v_1 is the rate at which the gas would evaporate if the surface were completely covered, θ_1 is the fraction of the surface covered at equilibrium and θ' the fraction covered in a time t . The left hand member of the foregoing equation corresponds to m in Formula 3 and should be a constant at constant gas pressure and temperature.

¹ An error in printing in Langmuir's paper gives the right-hand member of this equation, $1/t \log \theta'/\theta_1 - \theta'$.

Case 2.—Assume that the force of attraction between the surface and the molecules is active through a distance greater than one molecule thick, and that a fraction of a second layer is adsorbed. Second, let it be assumed that the ratio of the number of molecules condensing on the first layer to the number evaporating from the first layer is a constant. This will produce a second reaction of the first layer and proceeding with a different velocity. Such a condition is expressed by the equations

$$\left. \begin{aligned} dx/dt &= m_1(a - x) \\ dy/dt &= m_2(xF - y) \end{aligned} \right\} \quad (4)$$

where x is the amount on first layer in time t , a is the amount on first layer when t is infinite, m_1 is the constant of the first reaction, y is the amount on second layer in time t , m_2 is the constant of the second reaction, and F is a coefficient such that aF equals the amount on the second layer when t is infinite. Furthermore, $\lambda + \gamma = K$ and $a + aF = A$, the capacity factor. The solution of these equations give

$$(x + y) = a + aF + a \left[\frac{F(m_1 e^{-m_1 t} - m_2 e^{-m_2 t})}{m_2 - m_1} - e^{-m_1 t} \right] \quad (5)$$

The form of the $(\lambda + \gamma)$, t plot of this equation will be the same as the K , t plots of Equation 3 when F equals unity and m_1 equals m_2 . These conditions appear improbable, however, since a fast and a slow reaction is

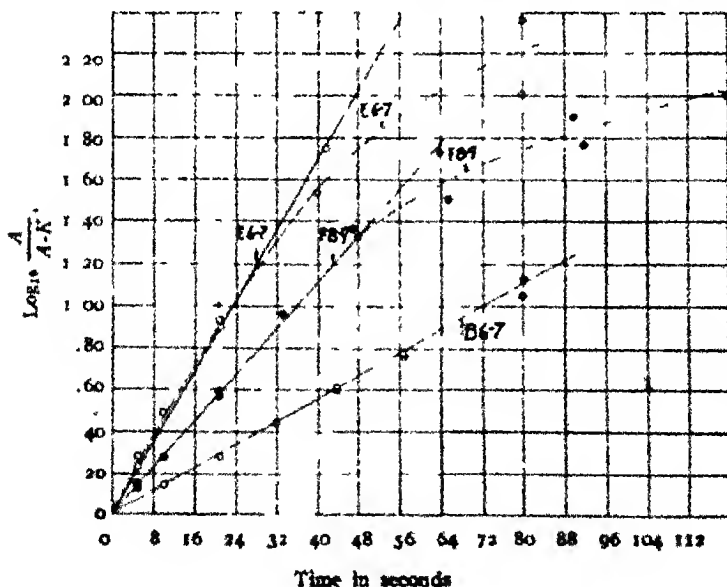


Fig. 2

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to be expected owing to the variation of the surface forces due to the successive layers. The form of the $(x + y)$ against t plot of Equation 5 will approach the form of the K, t plot of Equation 3 when F is small compared to unity and hence m_1 has many times the value of m_2 . To test these later conditions, accurate results must be obtained, especially near the end of the reaction.

Final Considerations.

To summarize one aspect of the results obtained in this investigation, it may be said that in all cases discordant and unreproducible values were always obtained except when the reaction was proceeding at the maximum

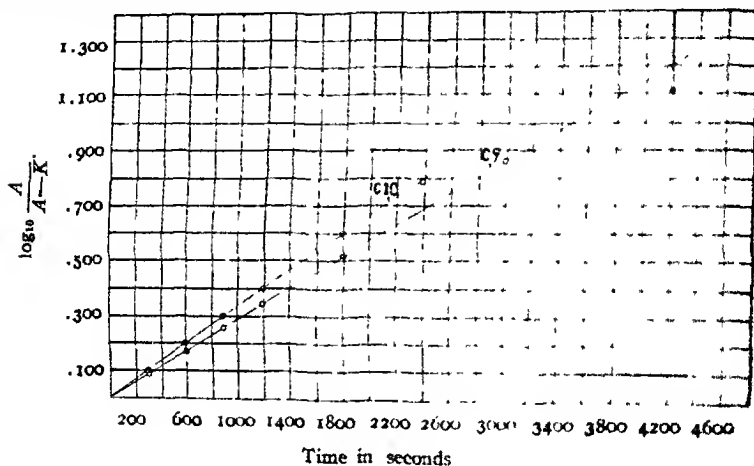


Fig. 9.

velocity obtainable under a given set of temperature and pressure conditions. When the maximum velocity was obtained, the reaction proceeded according to Equation 1 as shown by the figures in Table VII, and the plots in Figs. 8 and 9.

TABLE VII.

CCl ₄ NO ₂ B 6 $p = 59$ mm		
t (secs)	K	$m \times 10^4$
10	0.0901	1.49
21	0.1520	1.39
32	0.1963	1.36
44	0.2340	1.39
57	0.2556	1.33
80	0.2820	1.33
500	0.3083	
A	0.3100	

Mean, 1.38

CCl ₄ NO ₂ B 7		
t (secs)	K	$m \times 10^4$
10	0.0875	1.44
21	0.1473	1.33
32	0.1930	1.32
44	0.2328	1.37
57	0.2580	1.36
80	0.2862	1.40
A	0.3100	

Mean, 1.37

TABLE VII (continued).

CCl ₄ /NO ₂ C 9 $p = 0.61$ mm			CCl ₄ /NO ₂ C 10		
t (sec.)	K	$m \times 10^3$	t (sec.)	K	$m \times 10^3$
300	0.0532	3.00	300	0.0571	3.27
600	0.0948	3.00	600	0.1034	3.33
900	0.1250	2.87	900	0.1385	3.30
1200	0.1574	2.98	1200	0.1683	3.32
1800	0.1972	2.90	1800	0.2089	3.29
2400	0.2265	3.00	2400	0.2329	3.24
3000	0.2430	2.94	A	0.2800	
4200	0.2585	2.65			
A	0.2800				
Mean, 2.90			Mean, 3.29		
CCl ₄ /E 6 $p = 32.8$ mm			CCl ₄ /E 7		
t (sec.)	K	$m \times 10^3$	t (sec.)	K	$m \times 10^3$
5	0.0872	4.71	5	0.0805	4.88
10	0.1413	4.94	10	0.1284	5.03
21	0.1858	4.74	21	0.1637	4.31
42	0.2043	4.18 [*]	40	0.1826	4.07 [*]
A	0.2080		A	0.1870	
Mean, 4.83			Mean, 4.74		
CCl ₄ /F 8 $p = 5.8$ mm			CCl ₄ /F 9		
t (sec.)	K	$m \times 10^3$	t (sec.)	K	$m \times 10^3$
5	0.0583	2.97	5	0.0495	2.61
10	0.0941	2.76	10	0.0892	2.76
21	0.1460	2.72	21	0.1400	2.78
33	0.1782	2.90	33	0.1683	2.87
A	0.2000		A	0.1890	
Mean, 2.84			Mean, 2.75		

* Values determined near the end of the reaction are subject to considerable variation from the general mean. These values will be neglected in computing a mean value.

Referring now to plots in Figs. 8 and 9, it is seen that at pressures of 0.61 mm and 5.90 mm of chloropicrin, the $\log(A - K)$, t plots are straight lines, thus conforming to Equation 3¹. F-8 and -9 conform to the same equation up to very nearly the final capacity and then fall off in accordance with the slow secondary reaction of Equation 5. This is true to a greater extent with the results E-6 and -7 at a gas pressure of 32.8 mm. of carbon tetrachloride, as shown by the dotted line in Fig. 8 which is drawn through the points obtained. Although this deviation is not due to experimental error, sufficient data near the end-point have not been

¹ Others have pointed out that this reaction was probably monomolecular. Valentin (Beil. Ann. Physik., 40, 489 (1916)) Lamb and Finklestein were the first to study these adsorption velocities in the Chemical Warfare Service work. They found that the reaction followed closely the monomolecular law.

obtained to decide the matter. For the present, the slopes of the straight lines will be taken as the values of m . This may be regarded as an approximation and thus far all the above velocity data are, in general, in agreement with Langmuir's theory.

However, if only very minute quantities of gases retard the velocity of adsorption to the extent observed in this investigation, the above theory will have to be modified or further assumptions added. A further investigation of the quantity of foreign gas necessary to cause such lags is of great importance and is about to be undertaken.

The Pressure Effect.

(1) *On Velocity*.—Langmuir¹ has employed the formula

$$\mu = \frac{p}{\sqrt{2\pi MRT}} \quad (6)$$

for calculating the rate of bombardment of the gas molecules on a solid surface. μ is the number of gram molecules striking unit surface per second, m the molecular weight, T the absolute temperature, p the pressure, and R the gas constant in ergs per degree. Thus, for an ideal gas the rate of bombardment is proportional to the pressure.

Langmuir's equations give, where m is the constant of Equation 3

$$m = \frac{N_0}{N} v_1 \left(1 + \frac{\alpha}{v_1} \mu\right),$$

an expression which, combined with (6) will make m a linear function of the pressure. A sufficient number of reliable results have not yet been obtained to test this relation adequately. The 2 carbon tetrachloride measurements at pressures of 18.8 mm. and 32.8 mm., however, indicate that at these high pressures the velocity constant m is directly proportional to the pressure. The result on the other hand is quite different for chloropicrin since the pressure decrease from 5.9 mm. to 0.61 mm. or a 10-fold decrease, causes a 42-fold decrease in m .

(2) *On Capacity*.—Langmuir's Equation 9 gives

$$q = \frac{abp}{1 + ap}$$

for the relation between q , the total capacity, and p , the pressure where a and b are constants. This agrees with the large amount of evidence obtained by Langmuir on the adsorption of various gases at low pressures (2 to 100 bars) on glass and mica. Differentiation of the above gives

$$\frac{dq}{dp} = \frac{ab}{(1 + ap)^2} = 0, \text{ for } p = \infty$$

and hence dq/dp becomes smaller as p increases. At higher pressures

¹ Phys. Rev., 2, 332 (1913). Trans. Amer. Chem. Soc., 35, 129 (1913).

the capacity should vary little with the pressure. This conclusion is confirmed by the result with chloropicrin reported in this investigation. The capacity per g. of charcoal was 0.2800 g. at a pressure of approximately 5×10^3 bars and 0.3100 g. at 5×10^4 bars, an increase of only 10% in capacity with a 10-fold increase in pressure. The present data are, therefore, qualitatively in accordance with the one layer theory as regards the capacity.

The author wishes to express his appreciation to Professor Frederick G. Keyes of the Massachusetts Institute of Technology for criticisms and suggestions in connection with this work.

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

SOME PROPERTIES OF CHARCOALS.

BY H. E. CUDE AND G. A. HULETT

Received December 18, 1919

In a study of the moisture and gas content of various types of charcoals used in gas warfare we incidentally determined the densities of these charcoals.¹ It soon developed that it was by no means an easy matter to determine the true density of a charcoal for we soon discovered that there was a "drift" or increase in weight when it was immersed in a liquid. This drift decreased with time but was noticeable after weeks, and in some cases it was detectable after months. Furthermore, its magnitude was such that the first suggested explanations proved quite inadequate.

In determining the moisture and gas content of the activated chars, 5 to 10 cc. of the material was inclosed in a thin-walled glass tube with a capillary outlet, and the moisture and gases pumped out and determined. The charcoal was finally heated to 445° (sulfur b. p.), and the system was thoroughly out-gassed and the capillary sealed off. After the tube and charcoal were weighed, the capillary was broken under the liquid, a fine platinum suspension wire was attached to the tube, which was then immersed in the liquid and the whole was thereupon weighed. Finally the glass tube was weighed in air and also in the liquid, so that many corrections were eliminated in the density calculations. Temperature effects due to wetting the charcoal were found to disappear in some 10 to 15 minutes and weighings were then made at intervals. The weighings were made in a constant-temperature room, but the temperature of the liquid was also carefully followed. It was found that the weight increased markedly at first, then fell off with time. The following table will give an idea of the observations:

¹ War Gas Investigations, G. A. Hulett, C. W. S., Reports, September-December, 1918.

TABLE I.

Time	Weight of system in water G	Increase in Wt G	Volume change cu mm per g
0....	.. 3 5602		
5 min	... 3 5660	0 006	2 9
15 min..	. 3 5732	0 013	4 2
1 hour	.. 3 5854	0 0252	8 1
2 hours	3 5963	0 0361	11 7
9 hours	3 6130	0 053	17 1
19 hours	3 6177	0 0577	18 9
2 days	3 6234	0 0634	20 4
5 days	3 6285	0 0685	22 1
11 days	3 6313	0 0713	23 0
16 days	3 6315	0 0715	23 0

The final density of this charcoal was 1.850. By removing the external water from the pieces of charcoal, the weight less the mass of the charcoal gave the water in the capillaries, and the volume of these capillaries was found to be 0.42 cc. per g. In the case considered the "drift" was

5.5% of the capillary volume, other liquids have shown a drift of as much as 15%, with this charcoal.

The charcoals were pumped out with a large Toepler pump arranged for drying with phosphorus pentoxide (Fig 1). This pump collected the gases and also served as a MacLeod gage. The bulb held 1250 cc. and the fall tube was calibrated. It was possible to measure as little as 0.006 cc. under a pressure of 2 mm. in the upper part of this tube before it was run out. We thus knew the vacuum attained at any time. Most of the tubes were pumped out and sealed off at 445°, some at 218°, in the apparatus represented by Fig. 2, in connection with the determination of the mois-

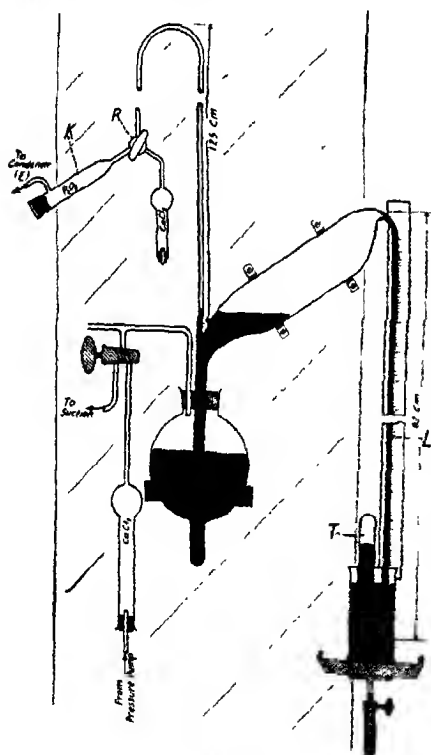


Fig. 1

these charcoals. Some tubes were connected directly to the pump with good phosphorus pentoxide drying tubes and pumped out while being heated to 520° in an electric heater. Also some of the samples were put into quartz tubes heated to 1020° , thoroughly outgassed at this temperature, and sealed off; but there was no noticeable difference in the drift with these different treatments. Above 200° the absorbed gases and vapors were readily pumped off from the charcoals, but a trace of gas (mostly carbon dioxide and monoxide) was given off, slowly for an hour or so before there was a decrease whereupon the char was soon pumped down to very low pressures. When a char was satisfactorily out-gassed at any temperature it was found that increasing the temperature yielded more gas. Some work on another phase of the charcoal problem, which we hope soon to publish, will give an explanation of this generally observed phenomenon. For the present we satisfied ourselves that there is no residual gas in our charcoals when opened under the liquids.

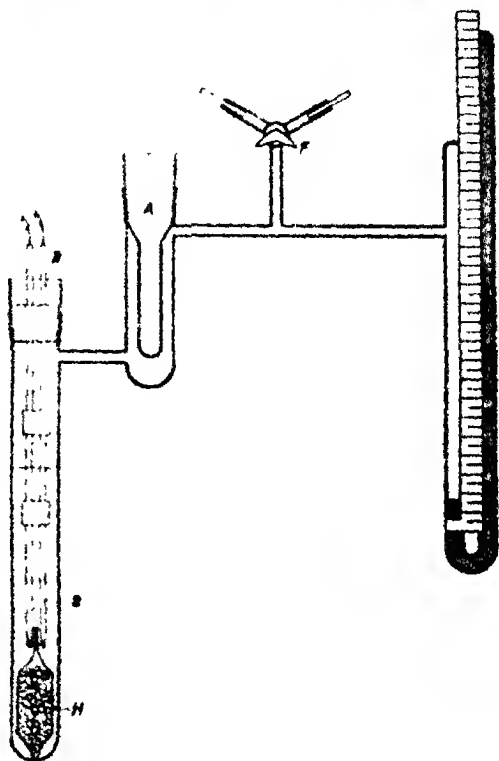


Fig. 2.

Figs. 1 and 2 will give the necessary details of the apparatus used in these experiments. The insert tube A (Fig. 2) was kept filled with solid carbon dioxide (-78°) so that any water froze immediately and was later removed and weighed in a special container. In order to manipulate the rods which carried the electrically heated wire, a rubber stopper was necessary. This stopper was sealed with marine glue into a ground glass collar B (Fig. 2) and was perfectly tight.

We have taken care to select well defined liquids and purify them, so as to avoid liquid mixtures or solutions which might

selective absorption of the heavier constituents and increase of weight with the time. We also paid particular attention to removing the dis-

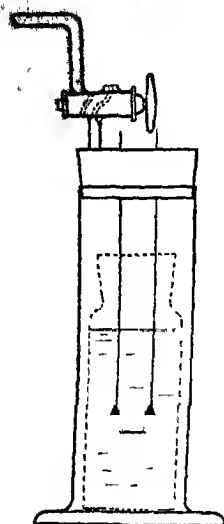


Fig. 3



solved gases from these liquids. This difficult problem was handled as follows: The liquid to be used was put into the glass bottle (Fig. 3), this bottle and liquid placed in the vacuum cylinder B and the tiny spiral (electrically heated) caused the liquid to boil while it was being pumped out. The cylinder was then opened and without disturbing the liquid the charcoal tube was introduced and the tip broken well down in the liquid. As soon as temperature effect had

disappeared a fine, platinum wire was attached to the tube and weighings were made.

Charcoals and other Absorbent Materials Used.—Most of the work was done on a cocoanut charcoal, made for the Army gas-mask canisters at the Astoria plant. A 5-gallon sample (A 909) and samples of 4 to 6, 8 to 10 and 18 to 20 mesh sizes were obtained. We also prepared a sample of 100-200 mesh size. In order to obtain a very fine material, the char was ground in a ball mill (Fig. 4) and a slow current of dry air passed

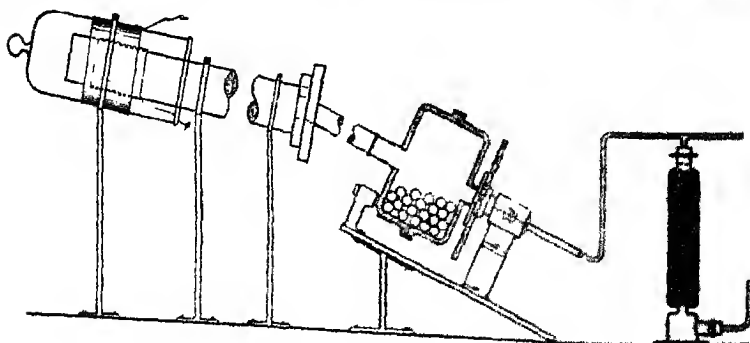


Fig. 4

through the mill and controlled so that only the finest of the material suspended in the air was carried along. This material did not settle in the 4-ft. length of wide glass tubing, so it was necessary to use a Cottrell precipitator at the end. A microscopic examination of this deposit indicated that the largest pieces were about 0.001 mm. in diameter. A given sample could be put through this mill with but little loss. We also had available some British gas-mask charcoal made from birch wood and some German charcoal from unused canisters of a late date. We also worked with spongy platinum and precipitated gold, and with some silica gel furnished by Dr. W. A. Patrick.

The Drift.—The increase in weight of the charcoal with time when opened under a liquid, has been plotted in the form of curves (Fig. 5). In order to allow temperature effects to disappear, the first observation was generally taken some 10 to 15 minutes after opening the tube in the liquid. An inspection of the first part of these curves indicates that a considerable part of the drift had already taken place before the first reading was made. Evidently the drift is due to the liquid penetrating the grains of the charcoal, rapidly at first—then more slowly. The only other explanation of a changing weight, while immersed in the liquid, would be to attribute it to a change in the shape or size of the grains of charcoal, but there has been no suggestion of this in any of the work; indeed, in some of the experiments described later we have subjected the whole system to pressures of several thousand atmospheres, which resulted in completing the drift at once, but there was no observable effect on the size or appearance of the charcoal particles. If there had been a change in the size of the grains of the order of magnitude of the observed drift, there would have been some settling of the charcoal in the tube; that is, a change in the apparent density of several per cent. In the absence of this it must be concluded that the increase in weight is the result of a gradual penetration of the liquid into the grains of charcoal.

Many questions now presented themselves, and one of the first considered was as to the extent of the drift with liquids other than water. To study this effect we selected liquids which differed widely from water in surface tension, viscosity, molecular volume and other physical and chemical properties. The following observations (Table II) are typical of the results. They were obtained with a uniform sample of charcoal (A 909), 18 to 20 mesh, and are plotted in Fig. 5.

TABLE II.

Liquid.	Time of drift Hrs.	Density after 15 min.	Density. Final.
H ₂ O.....	119	1.829	1.854
CS ₂	362	1.915	1.984
C ₆ H ₆	286	1.734	1.797
CCl ₄	2856	1.596	"

It is seen that the amount of the drift, the extent in time of the drift and the final density obtained vary widely with the 4 liquids under consideration. Other liquids tried showed values in the ranges here covered, but these liquids have not been as yet so thoroughly investigated.

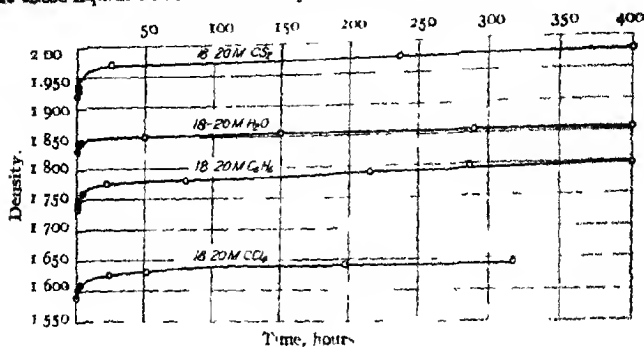


Fig 5

On opening a prepared tube of the char under a liquid the latter rushed in and filled the voids at once and completely surrounded each grain of charcoal. Also, all large pores must have filled immediately but it seems that the filling of the very fine pores is a slow process and is the main factor in the observed drift. The maximum observed density of the carbon of the char is above 1.9. A gram of this char has shown a capillary volume of 0.42 cc., so the block density of a grain of char would be about 1.07. The first observation with carbon tetrachloride gave a density of 1.60, some 70% of the 0.42 cc. of the capillaries had been filled, but this density was taken 15 minutes after opening the tube and a considerable amount of the drift had already taken place. One experiment with water gave many readings in the first part of the curve which permitted of extrapolation to zero time, indicating that about $\frac{1}{3}$ of the total drift takes place in the first 15 minutes. Vapor undoubtedly precedes the liquid into the capillaries but it must be rapidly adsorbed by the clean carbon surfaces in the capillaries of the charcoal and, in any event, could not impede the entrance of the liquid.

The forces acting to fill the capillaries are atmospheric pressure and capillary action. We may calculate this latter force from the relation between surface tension and the height to which a liquid will rise in a tube.¹ Pores 0.001 mm. in diameter would have a capillary force corresponding to 3 atmospheres, and 0.0001 mm. to 30 atmospheres, etc. Whether we are justified in extrapolating this relation to pores of molecular dimensions is questionable, but obviously this force is far greater than atmos-

¹ Bigelow and Bartells, THIS JOURNAL, 31, 1197 (1906)

phic pressure which, in our case, was constant, so we at once compared the surface tension of these liquids with the amount and extent of the penetration. Water has a surface tension of 72 absolute units while carbon disulfide shows only 34, but the latter showed much greater penetration and density. We must consider, however, that the viscosity of the liquid would be an important factor in the rate of penetration of these liquids into very fine capillaries and in determining the amount of penetration in experimentally realizable time. As a first approximation we have considered the penetration to be proportional to the surface tension of the liquid and inversely proportional to its viscosity, or more simply, to equal a constant times the product of surface tension and fluidity. The resulting numbers are: water, 7200; carbon disulfide, 9100; benzene, 4800; carbon tetrachloride, 2600. These numbers are entirely in accord with our observations on the drift and densities. The amyl alcohol number is 550 but we have only a few experiments with this substance as yet and they are around those of carbon tetrachloride. With capillaries of molecular dimensions the shape and size of the ultimate particles of the liquid must also be a factor, but this is the only relation we have as yet noticed between the drift and the physical properties of the liquids.

Attention may be next turned to the effect due to variation of the size of grains of the charcoal with a given liquid. Using this same A 909 charcoal, and water as a liquid, we secured the results given in Table

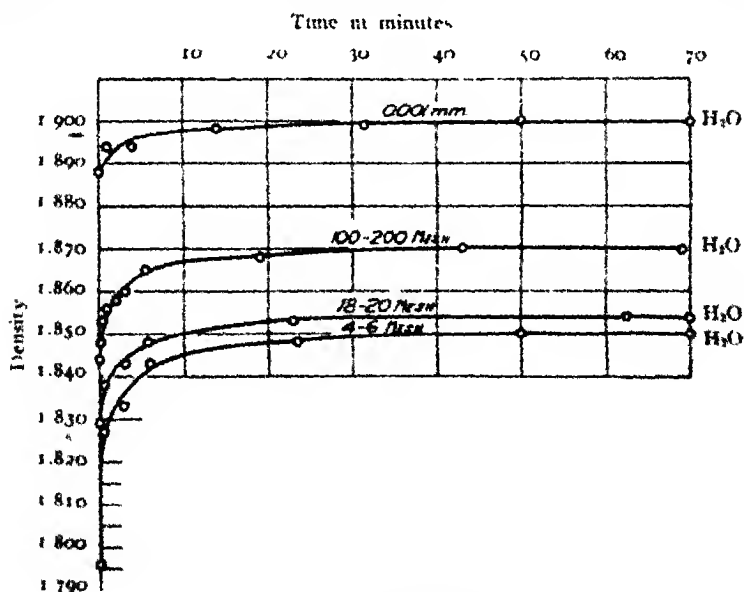


Fig. 6.—Drift in water.

III, and Figs. 6 and 7. For benzene with this same material the results are given in Table IV.

TABLE III

Size Charcoal mesh	Grain in mm	Time of drift Hrs	Density after 15 min	Density Final
6-10	1.95	227	1.751	1.845
18-20	0.71	119	1.829	1.854
100-200	0.165	74	1.844	1.870
	0.001	87	1.888	1.900

TABLE IV

Benzene

Size mesh	Time of drift Hrs	Density after 15 min	Density Final
6-10	743	1.695	1.785
18-20	286	1.734	1.797
0.001 mm	210	1.814	1.866

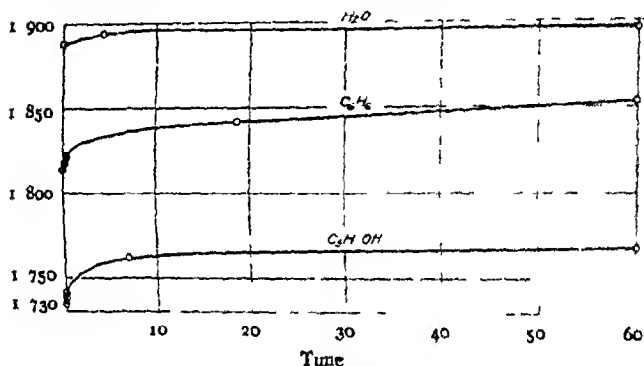


Fig. 7—0.001 mm. of substance

It is noticeable in these results that the extent of the drift and its duration decreased markedly with the size of grain. Also the final density increased with this factor. These effects have been noticeable with all of the liquids. Such results may all be readily interpreted from the standpoint that the liquids encounter mechanical difficulties in filling the small pores. The value we have obtained for the volume of the capillary spaces, 0.42 cc. per g. for this char, has been found to be quite independent of this size of the grains.¹

Breaking up the grains increased the surfaces and number of pores exposed per g. of char in the ratio of about 1 : 3 : 12 : 2000 for the

¹ This value was obtained first by using filter paper to remove the external water from the grains of char which had been completely filled with water, thus getting the weight of char filled with the liquid and subtracting the weight of the carbon. Later we found that this could be more easily done by centrifuging in a Gooch crucible (8 cm. X 1000 r p m). The results of different workers checked to 2%.

sizes 2 mm., 0.7 mm., 0.16 mm., and 0.001 mm. (6 to 10 mesh, 100 to 200 mesh and 0.001 mm.). The external surfaces of these size grains per g. are 0.003, 0.008, 0.034 and 5.6 square meters, respectively, while the surfaces in the capillaries are of quite another order of magnitude. Some results and calculations from vapor absorption work gives this area as less than 200 meters square per gram for this char. It will be seen, therefore, that the total surface available for adsorption is not materially affected by grinding, even when we were able to reduce the char to a powder whose largest grains were only 0.001 mm. in diameter. Our changes in drift and density are far more in accord with the changes in the external surfaces of the different sizes of grain than with the change in total surface of capillaries and external surfaces. Furthermore if 200 meters square per g. is the order of magnitude of the surfaces of the capillaries, a layer of liquid one molecule deep on this surface would represent a volume of some 20 cu. mm. If this adsorbed layer were in a condensed form and attained a greater density than the pure liquid, it still could lose only a part of its volume; if it enters into some chemical reaction with the carbon, due to residual valences, it would only contract to a portion of its volume as is evidenced by the decrease in volume when liquids and solids combine to form true compounds. Any explanation based on adsorption seems to offer little hope of explaining the drift which may, for this char, be as much as 50 to 100 cu. mm. Absorption may, however, play a secondary role. A calculation of the magnitude of the capillary force in causing the liquid to penetrate the pores showed that atmospheric pressure played only a secondary role in our experiments. Now, we have tried the experiment of applying external pressure to the liquid soon after the tubes were opened. We were not equipped for this work at Princeton, but the Geophysical laboratory of the Carnegie Institute most kindly allowed us to use their fine equipment for pressure work and we wish to take this opportunity to express our appreciation of the kindness and assistance of Messrs. L. H. Adams, E. D. Williamson and R. E. Hall in connection with the following experiments.¹

Tubes were carefully prepared at Princeton and carried to Washington for the pressure experiments. One containing 3.9587 g. of charcoal A 909 was opened under water and the first part of the drift carefully followed; the observation gave sufficient points to extrapolate to zero time. The plot of the results is found in the first part of the curve of Fig. 8. Using the extrapolated value this char had shown a drift of 75 mg. in 32 minutes from the time the tube was opened. The system was then subjected to a pressure of 500 atmospheres and kept at this pressure for 30 minutes. On removing the pressure and weighing the tube and char,

¹ For a description of apparatus see Adams, Williamson and Johnson, *THIS JOURNAL*, 41, 12 (1919).

an additional increase of 73 mg. was noted. The tube was now subjected to 1500 atmospheres pressure for 35 minutes which produced an increase of only 4.7 mg. The pressure was then raised to 9000 atmospheres, but there were indications of the water beginning to freeze, so the pressure was immediately lowered to 8600, which is below the freezing pressure of water for this temperature (19.5°), and this pressure was maintained for 50 minutes, but caused an increase in weight of only 3 mg.

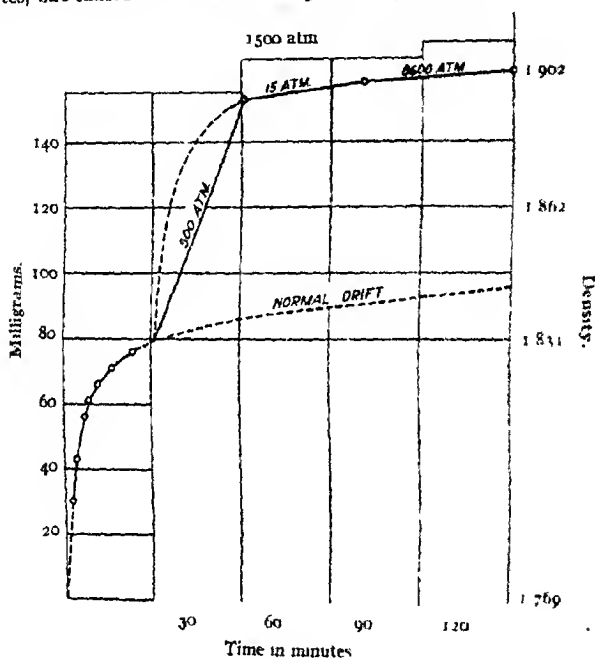


Fig. 8.

The dotted line (Fig. 8) presumably represents the drift while the tube was under a pressure of 500 atmospheres. It seems probable that the drift would have completed itself in a few hours under this pressure, and if further experiments confirm this supposition, moderate pressures will suffice to wipe out the drift in a few hours. This tube, immersed in water, was brought back to Princeton and weighed at intervals for 8 days but no further increase in weight was noted. The final density was 1.902 while we were getting for this charcoal immersed in water only 1.86 after 4 months. It would take years, at this rate, to reach the value obtained under pressure.

In some of the pressure experiments we weighed the charcoal in a few

minutes after the pressure was relieved and then at intervals for a few hours in order to detect a decrease in weight but in no case observed such a change, *i. e.*, water coming out of the char. In a few instances we did notice a slight increase in weight or still further drift. This happened when the pressure had not been applied long enough. A sample of this same char was opened under water and quickly subjected to a pressure of 3400 atmospheres for a half hour. This tube was then under observation for drift for 9 days but its weight under water did not change. We changed the temperature of this tube in water to 0° overnight and then to 50° for several hours, then on returning to room temperature the weight of the tube came back promptly to the previous weight. The water was now removed from this charcoal and it was pumped out and sealed off at 445°. When this tube was opened under water it showed the normal drift, became practically constant in 10 days and then showed a density of 1.878, while the density was 1.83 after the first 15 minutes. It would seem, therefore, that pressure will quickly complete the drift and give a definite final condition, and that the pressure does not destroy the drift property or noticeably affect the properties of the charcoal. A few pressure experiments were made with other liquids. The benzene tube was over pressed, froze and broke the tube. The amyl alcohol tube and the carbon tetrachloride tubes came through all right and showed final densities of 1.70 and 1.67, respectively.

We wish again to thank the staff of the Geophysical Laboratory for their assistance in carrying out these experiments which have given us a good idea of the possibilities along this line. Now that it is possible to get final results in a short time instead of waiting months, it will be possible to investigate a larger number of liquids and materials and test out the relation of the penetration of different liquids to their surface tensions, viscosities and other properties. Where the capillaries are of molecular dimensions, the shape and size of the ultimate particles of the liquid must also be a factor.

The authors wish to thank Mr. B. Peyton for assisting in the preliminary work on this problem.

PAINEBROOK, N. J.

[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH OF THE
UNIVERSITY OF PITTSBURGH.]

THE EFFECT OF SURFACE OXIDATION ON SOME METALLIC CATALYSTS.¹

By FRANK F. RUPERT.²

Received December 27, 1919.

A paper by Wigand entitled "The Increase of the Catalytic Action of Platinum on the Combination of Detonating Gas by Galvanic Polarization,"³ suggested experiments leading to a further development of Wigand's theme. A repetition of his experiments with a simple form of

¹ This paper describes part of an investigation made by the author in 1913-14 on the general subject of the relation of electrical potential to catalysis. The study of a number of phases of the general problem gave entirely negative results in practice, and full consideration of the theoretical bearings of the problem afforded no justification for its underlying premises. It was learned, however, that there are a few cases in which electrical potential and catalysis are indirectly related, although the connection may be accidental, and one of these cases, which forms the subject of this paper, was considered worthy of study on its own account. The work on the subject was discontinued when only approximate and partial results had been secured, but the publication of such data may at least call attention to some phenomena worthy of further study. Among the phases of the subject deserving further attention are the activity of the platinum metals other than those mentioned, a fuller comparison of the author's results with those of Sackur, and the thickness and properties of the oxide films.

The author wishes to acknowledge his obligation to Mr. Joseph Morwitz for valuable assistance and to Dr. E. W. Tillotson for helpful suggestions.

² Industrial Fellow, Mellon Institute.

³ *Sitzb. Ges. Naturw. Marburg*, 1907, p. 33.

On account of the brevity and inaccessibility of Wigand's report, the following translation is given:

"A letter from Wöhler (Göttingen) to Buß (Giessen) written in the year 1869 led me to conduct a series of experiments to explain the fact, also observed many other times, that the catalytic power of smooth platinum is considerably increased if it has been previously used as an electrode in a cell for the decomposition of water.

"In this preliminary paper information about the single experiments will be reserved until the quantitative relations are studied more exactly. The method of experimental procedure is as follows:

"In an eudiometer tube with electrodes of smooth platinum wire or foil, detonating gas is liberated from dilute sulfuric acid until the electrodes are completely surrounded by the gas. The connection with the battery is then broken. For several hours a gradual rise of the liquid is then observed, as a rule until the platinum is completely covered.

"This phenomenon is explained in this way; as the result of the preceding galvanic polarization the platinum is loosened at the surface and heavily charged with hydrogen and oxygen. The power of catalyzing the combustion of detonating gas is increased in much the same way as if the platinum were platinized until black. After being well purified and heated to glowing, smooth platinum possesses this catalytic power only in a small degree."

So far as ascertainable, no further results have been published by Wigand.

apparatus confirmed his results. The first object of the present investigation was to determine which electrode, if not both, acquires the increase in catalytic activity which Wigand found; next, it was desired to make the results quantitative, if possible, and the third aim was to determine the cause of the increased action. A number of secondary questions developed when the results of the experiments to be described were compared with those of Sackur.¹ The most important of these secondary questions was that of the activity of other metals than platinum, and several brief experiments on those metals were included. A few experiments were also made on another class of reactions, namely, the hydrogenation of oils.

Experimental.

Platinum.—For the purpose of deciding which electrode acquires most of the increased activity shown by Wigand's research, an H-shaped electrolytic cell was made containing a stopcock in the transverse tube. The electrodes consisted of rolls of platinum gauze in contact with platinum wires sealed through the bottom of the test-tubes. The cell was filled with 0.1 *N* sulfuric acid and was inverted over a vessel of the same solution. After passing a current of 0.1 ampere through the cell, keeping the stopcock open, until the tubes were nearly full of detonating gas, and allowing a minute for the diffusion of the gases, the stopcock was closed. It was immediately noticed that the gases combined more rapidly in the tube containing the gauze which had served as anode.

With the expectation of making quantitative comparison, and insuring thorough mixing of the gases, several other forms of apparatus were so devised as to permit accurate measurement of the volume of gas. The difficulty of obtaining quantitative results, however, was quickly demonstrated. Wide variations in the time required for recombination of the gases in any form of apparatus were attributed to such factors as slight impurities on the surface of the liquid and variations in the amount of liquid adhering to the metal. Qualitatively, however, the same result was obtained in practically every case; the use of platinum as anode in an electrolytic cell (with dil. sulfuric acid) caused a marked increase, while its employment as cathode produced no decided change in its catalytic power.

The final form of apparatus, with which most of the experiments were made, consisted simply of an eudiometer tube of 50 cc. or 100 cc. capacity, and a piece of gauze or foil of the metal under examination, usually 2.5 cm. square. In the experiments on platinum, the metal was, with the exception to be noted later, of the quality used in laboratory ware. After giving the metal the treatment desired for the individual experiment, it was rolled into cylindrical form and inserted into the closed end of the

¹ *Z. Elektrochem.*, 12, 637 (1906); *Z. Physik.*, 11.

eudiometer tube. The tube was then filled with distilled water and inverted over water. The detonating gas, which had been generated in a larger vessel, was delivered into the eudiometer tube as needed. The time of activation of the metal varied considerably in the earlier experiments, but 15 seconds was found to be sufficient to produce the maximum activation. As a rule, the electrolysis was continued considerably longer than 15 seconds, especially when the metal was used as cathode. The current density was variable, and was not measured in most of the final experiments, but in general the activating current was about 0.3 ampere. In order to correct the volume of gas for temperature changes, if necessary, a blank tube containing air was placed alongside the others.

The following, one of the most extensive series of experiments, gave results which were characteristic of all those performed:

The general plan of this series was to compare the activity of catalyzers before and after "cathodizing," (a word coined for convenience to denote using the metal as cathode) in a number of successive experiments, then to compare results similarly before and after "anodizing," i. e., using as anode. In each of 6 eudiometer tubes was put a piece of platinum gauze, 2.5 cm. square, using the method already described. All pieces of gauze used in the preceding experiments were cleaned with chromate mixture, then heated to redness, but not treated electrically. In the first few experiments the total contraction will be given for each tube at a number of readings. Tubes Nos. 1 and 2 were of 100 cc. capacity, the rest 50 cc. The first readings, taken as soon as possible after filling the tubes, follow:

0 = 9 34 A.M., Feb. 26, 1914

Minutes	Tube No.	TOTAL CONTRACTION, Cc						Average
		1	2	3	4	5	6	
15		0 50	2 10	1 90	3 70	1 30	5 10	4 9
30		6 45	3 70	3 36	7 05	27 25	11 03	9 8
45		8 91	5 25	4 70	10 48	36 20	17 23	13 8
60		11 45	7 00	6 10	13 97	47 30	23 59	18 2

A second set of readings, taken a few hours later, gave the following results:

0 = 1 20 P.M., Feb. 26

Minutes	Tube No.	TOTAL CONTRACTION, Cc						Average
		1	2	3	4	5	6	
20		2 80	3 55	1 80	2 56	6 70	4 05	3 3
40		4 90	6 32	3 50	5 45	14 07	7 97	7.0
60		6 80	8 70	4 65	8 16	23 95	11 90	10 7

The variations between the results with different pieces of gauze which were met with in all experiments, show the futility of trying to establish quantitative comparisons. Another set of readings at 4:30 P.M. gave an average rate of combination of 10.6 cc. per hour.

The next morning the following readings were taken:

0 = 9:07 A.M., Feb. 27.

Minutes.	TOTAL CONTRACTION, Cc						Average.
	1	2	3	4	5	6	
7.5	1.28	2.46	0.80	1.44	2.96	1.00	1.7
15	2.32	4.80	1.50	2.69	5.93	1.82	3.2
22.5	3.90	6.17	2.15	4.44	9.20	2.61	4.7
30	4.54	9.70	2.90	5.04	12.61	3.37	6.3

Average rate per hour 9.04 19.40 5.80 10.08 25.22 6.74 12.7

All gauzes were then removed, used as cathode in the activating cell one minute with a current of 0.3 ampere, then replaced in their respective tubes. The next set of readings follows:

0 = 10:20 A.M., Feb. 27

Minutes	TOTAL CONTRACTION, Cc						Average
	1	2	3	4	5	6	
10	0.94	1.70	1.57	1.38	1.73	1.25	1.4
20	2.14	3.78	3.27	2.77	3.65	2.80	3.1
30	3.32	5.92	4.97	4.28	5.09	4.36	4.8

Average rate per hour 6.64 11.84 9.94 8.56 11.38 8.72 9.5

After the tubes had stood until March 2nd and were refilled, the average rate was 6.35 cc. per hour. After one minute's cathodization the rate rose to 11.4 cc. per hour. After a second treatment as cathode the rate was 9.25 cc. per hour. On March 3rd, at 9 A.M., the rate was 8.5 cc. per hour before cathodizing and 10.5 cc. per hour after cathodizing. Another cathodization at 4 P.M. of the same day changed the rate from 9.0 to 3.7 cc. per hour. The rate continued low during the next three days, and several cathodizations had the usual uncertain effect. In all other experiments, the result of cathodization was likewise variable.

Just before the first anodization in this series, the following readings were taken:

0 = 1:23 P.M., Mar. 6.

Minutes	Tube No.	TOTAL CONTRACTION, Cc					Average.
		1	2	3	4	5	
20		0.60	2.96	3.02	0	0	1.1
48		1.30	7.08	7.21	0	0	2.6

Average per hour 1.62 8.83 9.01 0 0 0 3.2

After giving each gauze one minute's anodization and refilling the tubes, the following readings were taken:

0 = 3:00 P.M., Mar. 6.

Minutes.	Tube No.	TOTAL CONTRACTION, Cc					Average.
		1.	2	3	4	5.	
5	6.58	2.88	1.78	4.00	4.65	2.50	3.7
30	8.38	16.95	11.07	16.96	31.87	13.97	16 "
40	10.38	21.58	15.53	21.04			

In this experiment, the rate for the first hour was increased 8.5 times by anodization. Further readings showed a steady decrease in activity. At 9 A.M. March 7, when the rate had dropped to 6.8 cc. per hour, 5 minutes' anodization accelerated the average rate to 24.3 cc. per hour. The next day the result was substantially repeated. By March 10, however, further anodization no longer increased the rate, apparently on account of a film of grease which had reached the gauze.

In other series of experiments the order of the kinds of treatment was varied. There were often marked deviations between the results of individual experiments, but the bulk of observations led qualitatively to the same conclusion, that the use of the metal as anode very materially increases its subsequent effect on the rate of combination of detonating gas, while the effect of use as cathode is uncertain.

From a few experiments the further conclusion was tentatively established that the activity acquired on oxidation was lost on reduction, more slowly that it was acquired. A single experiment in which an *alternating current* was used in the activating cell gave the anticipated result, namely, a net increase in activity.

In a few experiments the usual piece of gauze was platinized, then treated similarly to the smooth platinum. The rate was always much greater than with smooth platinum. Use as cathode again gave uncertain results, but use as anode increased the rate of combination very materially, producing an explosion in one experiment.

It has already been pointed out that the platinum used was of commercial quality. Some experiments with a piece of c. p. platinum foil of the same size also showed increased activity after anodization.

Other experiments in which fresh pieces of platinum foil were used as *catalyzers*, before and after direct treatment with nitric acid instead of electrolysis, showed that the increase in activity is due simply to oxidation of the surface and is not peculiarly the effect of electrolysis.

Palladium.—This metal was selected next, on account of its great activity as a catalyst and its high adsorptive power for hydrogen. Some pieces of palladium foil of the same size as those of platinum were treated and used according to the methods already described. The rate of combination, always much greater than with smooth platinum under comparable conditions, was always increased by anodization, while the effect of cathodization was small and variable. When the metal was freshly oxidized, an explosion usually resulted within 2 minutes after filling the tube, while an explosion never occurred when the palladium had been heated immediately before the experiment, and rarely when it had been used as cathode or immersed in gaseous hydrogen.

Iridium.—The only specimen of iridium available at the time of the experiments was in the form of small lumps.

use these in the apparatus by attaching them to other materials. No catalytic activity was observed, but this result should not be regarded as conclusive.

Gold.—Gold foil, c. p., when used as catalyzer in the same apparatus, was found to have a catalytic power very much less than that of platinum but still noticeable. In one experiment with untreated gold 0.5 cc. of gas in a 50 cc. tube combined in 21 days. The effect of oxidation was very pronounced; in contact with the same piece of gold, anodized, almost the entire 50 cc. combined in 7 days. Anodization of the gold imparted a reddish color to the surface, followed by a change to greenish black when the metal was put into the reaction mixture. The surface, then, was greatly increased.

Cobalt.—Cobalt was the only other metal which was found to possess unmistakable catalytic activity for the reaction. The specimen of this metal was in the form of one cm. cubes and was not of known purity. Untreated, this metal combined 25 cc. of detonating gas in 90 days; anodized, it combined 50 cc. of gas in between 40 and 70 days. On anodization the solution immediately began to acquire the pink color of cobalt ion, and the surface of the metal became rougher.

Other Metals.—Experiments were also made with silver, copper, lead, tin, nickel, iron, chromium, tungsten, manganese, aluminum and bismuth. Two pieces of each metal were used, one untreated and one anodized. The first 4 mentioned were in the form of foil; the tin, aluminum and nickel were in sheet form, and the rest were in irregular pieces. All but the iron were of "c. p." grade. Each specimen of metal was inserted in an eudiometer tube and left in contact with the gas mixture for 3 months. To eliminate temperature effects, diffusion, catalysis by the glass wall, etc., two additional tubes without metal were filled, one with detonating gas and the other with air, and corresponding corrections were made. In some of the tubes a contraction was observed, amounting in the end to nearly $\frac{1}{2}$ of the total volume, and the residue proved to be largely hydrogen. Therefore, they were simply cases of oxidation of the metal. The manganese liberated some hydrogen from the water. There was no evidence of catalytic action by any of the metals in this series of experiments.

Hydrogenation of Oils.—The hydrogenation of certain vegetable and animal oils was chosen as another example of catalysis in which results might be of interest. The customary catalyst for such reactions is a finely divided metal or oxide, but it was expected that although the amount of hydrogenation with sheet metal as a catalyzer would not be great, sheet palladium would easily give measurable results.

Two series of experiments on the hydrogenation of cottonseed oil were conducted. The temperature in each experiment — — —

FRANK F. RUPERT

pressure 50 lbs., the time one hour, and the weight of oil 15 g, with a piece of smooth palladium 2.5 cm. square as catalyzer. In the first experiment in each series the palladium was heated before using, before the second it was cathodized until saturated with hydrogen, before the third it was anodized 10 or 15 minutes. The oil to be hydrogenated was contained in a small flask which was rotated horizontally within the pressure cylinder. The iodine number of the product was determined according to Wijs' method. In the following table of iodine numbers found, each figure represents the mean of two results which agreed within a few tenths of a unit:

	1st Series	2nd Series
Original sample	106.1	106.1
Untreated Pd	101.6	104.0
Cathodized Pd	101.4	101.4
Anodized Pd	81.5	81.0

The experiments were then repeated, with palladized palladium as catalyzer. The hydrogenation did not proceed as far as with the smooth metal, and the effect of oxidation, although noticeable, was much smaller. The product of hydrogenation, under the same conditions as in the preceding experiments, but using untreated palladized palladium as catalyzer, had an iodine number of 105; when the catalyzer had been anodized, the iodine number of the product was 103.4.

Similar experiments were made on castor oil, fish oil, seal oil and linseed oil, using smooth palladium and appropriate temperatures and pressures for each, but the hydrogenation found was always very slight. No effect on cottonseed oil was observed when sheet nickel was used as catalyst.

Discussion.

Wigand's theory that the increased activity is due simply to a loosening of the surface is disproved by the fact that no surface change was noticeable on anodizing, while in some of the earlier experiments a darkening of the surface was obtained by cathodizing with higher current densities than that usually employed, without very greatly increasing the activity.

The most reasonable possibility is, then, that the activity may be due to oxidation of the platinum. Several authors have noted that a small amount of platinum is dissolved or rendered soluble by oxidizing agents. Marie¹ found that if platinum is treated with strong oxidizing agents or used as anode in an electrolytic cell, then washed and treated with acids containing reducing agents, e. g., hydrochloric acid containing a small amount of potassium iodide, a small but measurable quantity of platinum

¹ *Compt. rend.*, 145, 117 (1907); 146, 475 (1908); *J. chim. phys.*, 6, 596 (1908). Complete references to earlier work by other investigators are given in the last mentioned paper.

is dissolved. In making quantitative measurements, the platinum was determined colorimetrically. Using pieces of platinum of various grades, 2.5 sq. cm. in area, as anode in dil. sulfuric acid and other electrolytes, for 30 to 120 hours, at a current density of approximately 4 amperes per square decimeter, Marie obtained 0.0005 to 0.0010 g. of platinum subsequently dissolved by the hydrochloric acid and potassium iodide, and found increases in weight of the anode amounting to 0.0001 to 0.0003 g. during the process of electrolysis. When a piece of platinum of the same total area was treated with any one of a number of oxidizing agents for a number of hours, the amount of platinum subsequently dissolved was about 0.00004 g. In both cases the extent of oxidation had apparently reached a maximum, due to the protective action of the film of oxide, which he believes to be of the formula PtO_2 . In some of the experiments a slight brownish color was noticed.

The author calculated the thickness of the film of oxide or rather of the platinum which had become soluble, using Marie's figures, on the assumptions that the surface is smooth and the thickness of the film is uniform. From the above figures and the density of platinum, 21.5, we obtain in the case of electrolysis:

$$\frac{0.0007(\text{av.})}{21.5 \times 25} = 1.3 \times 10^{-6} \text{ cm.},$$

and in the case of treatment with oxidizing agents.

$$\frac{0.00004}{21.5 \times 25} = 7 \times 10^{-8} \text{ cm.}$$

The atomic diameter in solids according to a number of investigators is 2 to 3×10^{-8} cm. Therefore, the soluble film formed by treatment with oxidizing agents has the thickness of two or three atoms, or possibly of only one atom, as the surface may not be entirely smooth and may be actually greater than that found by direct measurement. The conditions at the surface of the metal, if the layer is only one atom thick, are identical with those observed and discussed by Langmuir.¹ The thickness of the film after prolonged electrolytic treatment, however, amounts to that of 30 or 40 layers of atoms, so in that case there may be some loosening of the surface before a fully protective film is formed. The author did not determine the thickness of the film after the brief electrolytic treatment in his experiments.

According to Marie, surface oxidation of platinum by chemical or electrolytic means gives to the surface layer some of the properties of platinic oxide which he enumerates. To his list is to be added the property of catalytic power greater than that of metallic platinum, easily evident even when the film is of little more than atomic thickness.

¹ THIS JOURNAL, 38, 2267 (1916)

This conclusion is not in agreement with that of Sackur,¹ who deduced from a number of experiments on residual currents and on the amount of gases given off on electrolysis when different metals as electrodes, that the catalytic power of metals is decreased by negative polarization and increased by positive polarization. According to his view, oxygen acts on platinum as a poison, and the more easily a metal becomes passive, the lower is its catalytic power. The conditions in the author's experiments differ in many aspects from those in Sackur's; it must be noted, however, that the reactions in both cases take place in aqueous solution; in the one case in a thin film, and in the other in a large volume. On consideration of Sackur's deductions, without repeating his experiments, no tangible ground for adverse criticism of most of his conclusions was presented, but the mass of direct evidence in the author's experiments points to the opposite conclusions.

According to Sackur, the order in which the metals studied stand with respect to their catalytic activity toward the combination of hydrogen and oxygen, beginning with the most active is: silver, platinum, copper, lead, tin, nickel, chromium. Gold and the other platinum metals were not included in his experiments. According to the author's results, the order is palladium, platinum, cobalt, gold, with no indication of activity by any other metal studied. The activity of palladium is increased by surface oxidation for apparently the same reasons as is that of platinum. The activity of gold is increased in a higher ratio, on account of the formation of a non-protective coating of oxide, which is later reduced to the finely divided metal. The increased activity of cobalt is apparently due simply to etching and increase of surface. An estimation of the comparative order of magnitudes of the activities of the metals used gives 50 to 1 for the ratio of palladium to platinum; 2000 to 1 for platinum to gold, and 200 to 1 for platinum to cobalt.

Summary.

1. The catalytic activity of platinum and of palladium toward the reaction between hydrogen and oxygen at ordinary temperature in the presence of a film of water is increased by surface oxidation of the metal, whether accomplished by anodic polarization or by chemical means.
2. This surface oxidation consists in the formation of a film of surface-combined oxygen of little more than atomic thickness, whereby the surface acquires some of the properties of an oxide of the metal.
3. The catalytic activity of smooth palladium toward the hydrogenation of cottonseed oil is increased by surface oxidation.
4. The effect of cathodic polarization or hydrogenation on the catalytic activity of platinum and palladium is slight and uncertain in direction.

¹ *Loc. cit.*

5. The order of activity among the metals tested, beginning with the highest, is: palladium, platinum, cobalt, gold, with large differences in the order of magnitude of the activity. The activity of a number of other metals is too small to be discernible. The activity of gold is increased by surface oxidation, largely on account of increase of surface.

6. The results obtained are at variance with Sackur's conclusions with regard to the passivity of these metals and of hydrogen.

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ANALYTICAL WEIGHING.

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Introduction.

It appears that many chemists at the present time regard the use of long swings of the analytical balance as the best and most accurate method of weighing. Many recent text-books on quantitative analysis advocate this process, sometimes without even mentioning a simpler method, and the teaching of long swing weighing has evidently grown in favor in recent times.

While admitting that the use of long swings of the balance is capable of giving results that are accurate enough for ordinary purposes, the writer has absolutely no doubt that this practice is generally somewhat less accurate than the ordinary, simple method of using short swings. The very serious objection to the method of long swings, however, is that it is more difficult and much slower than the common method.

The object of this article, therefore, is to discuss methods of weighing, to present a plea for the general use in teaching and in practice of the simple, easy and accurate process of weighing with short oscillations of the balance, and for the abandonment of long swing practice, which evidently involves a great waste of time and labor, with no gain, but probably some loss, in accuracy.

The advocates of long swing weighing usually recommend the finding of a "zero-point" of the empty balance—a point not coincident with the zero of the graduated scale—in connection with each weighing, thus largely increasing the burden of labor in their otherwise cumbersome process. It is believed that this practice should be given up, no matter what method of weighing is employed, in favor of using the apparent zero of the balance as the basis of weighing, according to the old and reliable custom; for it is certain that when we weigh by difference, as we almost invariably do, the point of equilibrium of the empty balance is of no consequence, provided

that the adjustment does not change between two weighings required to find a difference.

Long Swing Weighing.

Since the analytical balance, when near equilibrium, does not readily give long swings, those who employ extensive oscillations usually obtain them either by fanning one of the pans, by temporarily applying the rider, by suitably manipulating the pan-arresters or by using a point of equilibrium at a considerable distance from the center of the graduated scale.

The last of these devices is adopted in a well known text-book¹ which does not even mention the use of short swings. The directions given in this book for weighing a crucible are copied here as a striking example of how weighing should not be done.

"In making a weighing one should always accustom himself to note the observations methodically, as follows

Assume that a platinum crucible is to be weighed

Zero point		I Point of rest with load of 12.052 gms		II Point of rest with load of 12.053 gms	
Left	Right	Left	Right	Left	Right
4 2	17 6	5 8	18 7	3 5	15 8
4 6	17 1	6 2	18 3	3 8	15 4
5 1		6 6		4 2	
Sum = 13 9	34 7	18 6	37 0	11 5	31 2
Mean = 4 63	17 35	6 2	18 5	3 83	15 60
	4 63		6 2		3.83
Sum of both means =	21 98		24 7		19.43
Mean	10 99		12 35		9 71

Sensitiveness = $12.35 - 9.71 = 2.64$ scale divisions

$12.35 - 10.99 = 1.36$ scale divisions

$1.36 \div 2.64 = 0.5$ mgm

Weight of crucible = $12.052 \pm 0.005 = 12.0525$ gms."

Fifteen observations of swings, much book-keeping, 9 calculations of mean values, 2 subtractions and finally a division and an addition are required here to finish weighing a crucible after getting within one milligram of the result. It would seem that gravimetric analysis would often be regarded as an unattractive occupation by students obliged to do all this and to repeat the performance after igniting a precipitate in the crucible. By the use of short swings in connection with the center of the balance, it would be easy to finish such a weighing, just as accurately, in about 15 to 30 seconds, by making 2 or 3 trials with the rider.

After all the labor recommended by Treadwell the result is expressed only to the nearest tenth of a milligram, and it is safe to say that if another decimal figure were calculated in such a case it would probably have little or no significance. It is fully believed that the quick method is

¹ "Analytical Chemistry," by F. P. Treadwell Translated by Hall.

rather more accurate than the enormously longer and more complicated one.

Treadwell shows the use of 3 readings on one side and 2 intermediate ones on the other side for finding each position of equilibrium, but it should be mentioned that some other advocates of long swings shorten the operation somewhat by employing 3 instead of 5 readings, while still others make the process longer by the use of 7 or more observations for each position.

An example of directions for using 7 readings in finding the "zero-point" is copied here from a very recent book by George McPhail Smith.¹

Left	Right
-6 8	+4 7
-6 6	+4 5
-6 4	+4 3
-6 3	
- -	- -
Average. -6 5	Average +4 5 Zero-point = -1.0

It may be remarked that, if it should ever be desirable to find such a zero-point when weighing by difference, it could be much more easily done by using short swings. For, with the point of equilibrium at -1.0 , a careful release would cause the needle to travel, after its first excursion, from -2.0 to 0 , or it might show slight variations from this, such as $-2\frac{1}{4}$ to $+\frac{1}{4}$ or $-1\frac{3}{4}$ to $-\frac{1}{4}$, etc. A glance at these swings would show their middle point with accuracy, and the observation could be repeated upon succeeding swings as often as desired.

De Konink² has gone so far as to recommend as many as 15 or 17 observations for each careful weighing with long swings, on the grounds that it is difficult to make the readings accurately and that numerous observations diminish the error. The writer does not believe that this exceedingly laborious plan is as accurate as careful short swing weighing.

The use of long swings appears to be an old process, for a description of it in 1864, in practically its present form, has been noticed.³ Its use may have been fully justified with primitive balances not provided with riders and with the tendency to give very long swings, but its application to modern analytical balances is believed to be a very different matter.

Short Swing Weighing.

There are some variations in the practice of those who do not finish their weighings by the use of long swings and indirect calculations, but

¹ "Quantitative Chemical Analysis," New York, 1919, p. 11.

² "Chimie Analytique," Liège, 1894.

³ "Handwörterbuch," by Liebig, Poggendorff and Wöhler, Fehling's Edition, Vol. 9, p. 493.

weigh quickly and directly by bringing the rider to the proper point and observing it.

Substances are almost always weighed by difference in crucibles, weighing tubes or other containers, with the use of the same apparent condition of equilibrium for any two weighings required to find a difference, and without any particular regard for the actual condition of the empty balance, provided that this remains constant. Of course, when substances are weighed directly upon the pan, as in the case of gold and silver assaying, it is necessary to have the empty balance carefully adjusted.

The swings generally used are so short that their retardation is inappreciable in a single movement, and hence the middle point corresponds with the point of equilibrium. They may thus vary from a maximum total length of about 4 divisions of the graduated scales of our American balances down to the shortest ones that are distinctly visible. The writer prefers very short swings, from $\frac{1}{2}$ to 2 divisions in total length, for final observations, because their retardation is inappreciable even after several repetitions, and because the central points of such short swings can be very accurately found by observations. However, this preference for rather short swings does not involve the recommendation that the natural swings of the balance should not be generally used, nor that anyone should employ swings that are too short to be easily and clearly observed without the suspicion that the motion may have stopped.

It is the most common practice, and the one preferred by the writer on the grounds of convenience and accuracy, to employ the center of the pointer-scale as the final middle point of the swing in finding equilibrium. Sometimes, however, a point of reference slightly distant from the center is employed, especially with assay balances, some of which may not swing at all when released in perfect equilibrium with the center, but not necessarily with our analytical balances, which seldom fail to give a sufficient swing, no matter how carefully they are released.

The writer has been informed by his former colleague, Professor Bahney, that the device of employing a single, outward swing, from the center to a definite point, about three divisions away, as the final indication of equilibrium, is very extensively used with assay balances, and, further, that this plan, following his own suggestion, has been applied exclusively and satisfactorily to analytical balances in a very large technical laboratory. Practically the same device, under the name of the "Single Deflection Method," has been described just recently by Brinton,¹ who states that it is an old process of unknown origin (it appears probable that it came from the assayers), and who has found that it gives excellent results, but has some limitations on account of the unsuitable release of certain balances. This method appears to be a very good one, especially

¹ THIS JOURNAL, 41, 1151 (1919).

for rapid technical weighing, but it is probably not quite as accurate as the use of short swings across the center, because it is possible for the release of the pans to impart a slight impulse to the balance and thus slightly shorten or lengthen the single outward swing.

It is customary to put weights upon the balance systematically by the trial of loads that are nearly midway between excesses and deficiencies, but as soon as the pointer, when carefully released, does not swing beyond the limits of the scale, the weighing may be finished very quickly by observing the extent of this outward excursion and thus finding, from the known sensitiveness of the balance, the exact, or almost exact, point at which the rider must be placed. Not more than one or two further trials are then usually needed to finish the weighing. Occasionally the excursions of the pointer, just referred to, are very long ones, and it may be remarked that this is the only kind of long swing observation that is approved of in this article.

Analytical balances are frequently so adjusted that their sensitiveness amounts to a swing of 5 divisions for one milligram, corresponding to $\frac{1}{2}$ division for 0.1 mg. With this condition of delicacy, therefore, a swing that varies less than $\frac{1}{4}$ division on the two sides of the center shows that the nearest tenth of a milligram has been found, and, since this is the usual limit of accuracy desired, the weighing is then finished.

It is not worth while to attempt to push the accuracy of ordinary analytical weighing beyond the limit just mentioned, either by reading the short swings with greater accuracy or by adjusting the balances to greater delicacy, because weighing to the nearest tenth of a milligram is usually the most accurate feature of an analytical process, and also because the balance is likely to display erratic behavior when extreme refinement is attempted, on account of changes of temperature, jarring or other causes.

Even in ordinary weighing, the greatest precautions should be taken in regard to temperature, for unless everything that it weighed is at precisely the temperature of the balance the errors may amount even to milligrams. The rapid increase in weight of a slightly warm object as it stands upon the balance is sometimes incorrectly attributed to hygroscopic behavior. The writer has heard the complaint that the asbestos in a Gooch crucible was hygroscopic, when the crucible had been weighed before it was quite cold.

Those who require weighing of the greatest accuracy, for atomic weight determinations or other purposes, must take the greatest precautions, such as the employment of a highly sensitive balance, making corrections for the buoyancy of the air, and making allowances for the errors in the sets of weights used. Such refinements, however, are usually out of the question in ordinary analytical work, because such work usually lacks the accuracy in other respects that would make such corrections reason-

able, and the ordinary busy analyst cannot afford the time and labor for immaterial things. All careful analysts, however, should be sure that their weights are good ones, and, if particular care is desired, sets of assay weights from one gram down can be procured, the errors in which are entirely inappreciable on an analytical balance. An assay balance is very suitable for testing such weights. As the weights above one gram are frequently inaccurate, it is best, in careful work, to use them merely as counterpoises, without changing them when weighing by difference.

Short swing weighing, with certain modifications, is very extensively employed with satisfactory results, and some of the most important works on quantitative analysis do not mention the method of long swings. Fresenius (1875) describes the point of equilibrium as the place where the needle will come to rest after swinging. Adolphe Carnot (1898) says that the equilibrium of the balance is indicated by the pointer oscillating equal distances on each side and finally stopping at zero. Neither Fresenius nor Carnot say definitely that we should wait for the pointer actually to stop, and it would evidently be more convenient to observe the middle point of short swings. Clowes and Coleman (1914) state that consecutive swings to the right and left must finally be equal in extent. It is evident in the last case that the swings, in order to be equal, must be short ones.

Arguments Against Long Swings.

There can be no doubt that these swings are used in the belief that they increase the accuracy of weighing, but there appears to be absolutely no theoretical or practical ground for this belief, for the following reasons:

1. A long swing shows no greater variation than a short one for the same difference in weight. The variation is an absolute distance, which is not proportional to, nor increased by, the length of the swing, because the balance acts as a pendulum and, except for retardation, the pointer must swing equal distances on each side of the point of rest. For example, if the point of equilibrium is at $+0.2$ the pointer should swing from 0 to $+0.4$ and from -0.5 to $+0.9$, and were it not for retardation, it would swing from -5.0 to $+5.4$, from -10.2 to $+10.6$, etc., where, in every case, the excursion is 0.4 greater on one side than the other, with equal distances from the point $+0.2$. There is no doubt that the difference, 0.4 , could be more readily observed from the short swings, 0 to 0.4 and -0.5 to $+0.9$, than from the long ones in which retardation prevents direct observation.

2. The retardation of long swings is such that their middle points do not coincide with their points of equilibrium, so that the latter must be found indirectly by calculation. Since the retardation is practically proportional to the length of the swings, it becomes inappreciable in a single, moderately short swing, or even in several shorter ones, so that the middle points of these correspond to their points of equilibrium, and the latter can be found very easily and accurately by direct observation.

There is no doubt that the direct, accurate observation is better than the indirect calculation.

3. Long swings cannot be read as accurately as short ones, because the more rapidly moving pointer in the first case allows less time for the careful observation of the end-point, and also because the parallax due to unsymmetrical positions of the observer's eye is much more likely to affect the reading of long swings than of short ones. Furthermore, the observation of very short swings across the center requires only the direct comparison of the two distances on each side, and this comparison can be made with great ease and accuracy. For instance, a swing from $+0.2$ to -0.3 could be readily seen to be unsymmetrical with the center, and the observation would be repeated and confirmed upon a number of succeeding vibrations, whereas this variation of 0.1 division could hardly be determined with certainty with long swings on account of the difficulty of reading them accurately, and because of the complication of retardation. It should be mentioned that a variation of 0.2 division in the swing indicates a difference of less than 0.1 mg. as balances are commonly adjusted; hence with an adjustment as sensitive as this a variation of 0.1 division, just discussed, or one even twice as great, could be disregarded in ordinary weighing.

4. There is no advantage, as far as diminishing the probable error is concerned, in the finding of the mean values of several observations that is practiced in long swing weighing; for when short swings are employed the final result is observed at once, and this can be compared with subsequent swings which are usually identical and confirmatory. In order to obtain similar comparison and confirmation, it appears that the long-swing operator should repeat the whole of his observations and calculations a number of times, and compare the series of results thus obtained.

5. The calculation of the point of equilibrium from long-swing readings is mathematically inexact, because the retardation diminishes with the extent of the swings, while the means of the readings on each side are used in the calculation. It is admitted that the error thus introduced is ordinarily inappreciable, but this would not be the case with a balance adjusted to unusual sensitiveness, or carrying a very bulky object, so that the retardation amounted to a rather large proportion of each swing. For example, supposing the retardation of each swing to be $\frac{1}{4}$ of the distance from its starting point to the center, the latter being the point of equilibrium, the long-swing readings to be expected might be $+10.0$, -7.5 , $+5.6$, -4.2 and $+3.2$, which give by calculation the point of equilibrium $+0.4$ instead of the correct point, 0 . On the other hand, short swings $\frac{1}{10}$ the length of the others would give the readings $+0.5$, -0.4 , $+0.3$, -0.2 , and $+0.2$, which would indicate the true point by calculation, or more simply by observation.

6. There is more probability of making accidental errors in weighing with long swings than with short ones, for the reason that there are numerous different readings to be made and recorded in the long-swing operation, any one of which if incorrectly found will affect the result, whereas in short-swing weighing the observation merely consists in reading the position of the rider after making sure that the short swings are almost equal on each side of the center. Then there are chances for errors in the complicated long-swing calculations, and these are not required with short swings.

7. There is no reason to suppose that long swings are in any way more reliable than short ones. It might be imagined, perhaps, that an old balance with blunted knife-edges or grooved bearings, or both, would give better long swings than short ones, but experience with a great many balances, some of which had been used by students for many years, has not disclosed any such case, and if such a balance should be found it would seem best not to use it at all.

8. Some readings of long swings made by the writer have shown considerable irregularity, and it was suspected that the currents of air set up by the swinging were a source of error. However, more careful experiments carried out with an excellent Becker balance, and with the aid of a magnifying glass, showed that the suspicion was probably groundless, and that the previous irregularities had been caused by errors in reading the long swings. In one instance, a 4-inch watch glass, used on account of presenting a large surface for stirring the air, was counterpoised upon the balance, and the swings $+0.3$, -0.3 , $+0.3$, -0.3 , $+0.3$ and then $+11.9$, -11.4 , $+11.0$, -10.5 , $+10.0$ were obtained, giving the indicated middle points 0 and 0.02, respectively. In another experiment the empty balance was adjusted to equilibrium at the center, long swings were started and readings were made until the oscillations had died down to short ones. The first 5 readings were $+12.0$, -11.7 , $+11.3$, -10.9 , $+10.6$, indicating that zero-point precisely, then, after 96 very satisfactory readings that will not be recorded here, the following were obtained: $+0.7$, -0.7 , $+0.7$, -0.7 , $+0.6$, -0.6 , $+0.6$, -0.6 , $+0.6$, -0.6 , etc. Both comparisons show excellent, and perhaps unexpectedly good results with the long swings, in the reading of which no high degree of accuracy can be claimed, but there is no indication of any advantage in the long swings over the short ones, and it is evident that the latter are much more convenient for reading and for finding the result.

Conclusion.

If the arguments presented here are sound, as they appear to be, it is certainly very remarkable that many chemists have considered it desirable to force the reluctant analytical balance, when close to equilib-

rium, to give long swings, in place of its natural short ones, in order to do a vast amount of useless work. The suspicion is unavoidable that the simple pendulum principle of the balance has been lost sight of in the entirely false expectation that the absolute variation of a swing would be increased by lengthening it. Possibly it has been supposed that short swings would be more likely to stop or to be erratic than long ones, but this is contrary to the very great amount of experience of those who use short swings, and it is contrary also to the precepts of high authorities, such as Fresenius and Carnot, already alluded to in this article. There is little doubt that many have merely followed the example of others in adopting this astonishing practice, without due consideration of the matter, and perhaps the mathematical and physical aspects of the method, or possibly its spectacular features, have had some influence in leading to its adoption.

It is to be hoped that all recommendations of long-swing weighing will soon disappear from our text-books of quantitative analysis, so that our future workers in chemistry may not be in danger of being burdened with a preposterously laborious method.

The writer is indebted to his colleague, Dr. John Zeleny, Professor of Physics, who has kindly examined the arguments presented in this article and has approved of its main conclusions in regard to long and short swings of the balance.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE AQUEOUS PRESSURE OF SOME HYDRATED CRYSTALS. OXALIC ACID, STRONTIUM CHLORIDE AND SODIUM SULFATE.

BY GREGORY PAUL BAXTER AND JOHN ERNEST LANSING.

Received January 17, 1920.

Information concerning the aqueous pressure of hydrated crystals is in an unsatisfactory state, partly because the different methods used have not yielded concordant results, and partly because no systematic attempt has been made to cover the ground thoroughly, so that data in this field are meagre. Yet, a knowledge of aqueous pressure of crystals is often desirable, for either theoretical or practical purposes, such as the determination of conditions under which hydrated crystals are stable. The present investigation was undertaken chiefly for the purpose of perfecting a reliable method of measuring aqueous pressures of crystals, although the data obtained may possess some intrinsic value.

The "air current" or "transference" method which was chosen, has frequently been employed for the purpose in the past, but as the results

obtained have been on the whole unsatisfactory, this method has acquired an undeservedly bad reputation. We have found, however, that with suitable precautions very uniform and satisfactory results may be obtained.

One of the chief difficulties has been due to the fact that the transition from a more to a less hydrated phase frequently does not take place unless the original substance is scratched or crushed or, best, inoculated with the less hydrated phase. An important precaution is, therefore, to mix intimately by grinding the more hydrated and a considerable proportion of the less hydrated phase. The presence of the latter substance is of further advantage in absorbing any excess of water coming possibly from pockets of mother liquor in the crystals or other sources. Beyond this precaution those involved in the accurate determination of moisture are necessary.

The experiments described in this paper were carried out with the 3 systems following: oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{C}_2\text{O}_4$), strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{SrCl}_2 \cdot 2\text{H}_2\text{O}$), and sodium sulfate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4$). These substances were purified by one crystallization and then were air dried. Some of the oxalic acid was heated to 100° for some time to expel the crystal water and then was intimately mixed with 10 times its weight of hydrated crystals by comparatively fine grinding. Considerable portions of the strontium chloride and sodium sulfate were exposed for some time in a vacuum desiccator over sulfuric acid and were then intimately mixed with from 10 to 20 times the amount of hydrated salt. The mixtures, interspersed with glass beads, were packed in large U-tubes which could be closed with ground joints and stopcocks, and were allowed to stand for some time before use, so that equilibrium might be established. The column of beads and substance was about 1.5 cm. in diameter and 30 to 40 cm. long, and was immersed to a considerable depth in the thermostat.

The method of experimentation was to pass a measured volume of dry air over the substance at constant temperature into a weighed tube containing phosphorus pentoxide, and finally into an aspirator bottle, in which the volume of air was determined. In order to purify and dry the air it was passed over silver nitrate solution, fused potassium hydroxide and conc. sulfuric acid, all contained in a system of large, glass-drying towers. The phosphorus pentoxide had been freshly sublimed in a current of oxygen, and was mixed with a considerable proportion of beads in the absorbing tube to prevent clogging. The absorbing tube was provided with glass stopcocks for the protection of the pentoxide when the tube was not in use. Great pains were taken that the moist air should always enter the pentoxide tube from the same side, so as to avoid the evaporation of the moisture from the end of the tube nearest the outlet.

The pentoxide tube was always weighed by substitution for a counterpoise similar in material, shape, and volume, and during the actual weighing of both the pentoxide tube and its counterpoise, one stopcock was always open in order to avoid irregularities from changing atmospheric conditions.

The volume of air passed over the salt was found by measuring the water run out of the aspirator in a large bottle, the volume of which had been determined very carefully by weighing its water content. At the beginning of the experiment the aspirator was always filled to the top with water, which had been allowed to come to room temperature before the air current was started. Thus no change in the volume of the water could take place during the experiment. The volume of the connecting tubes between the saturating tube and the aspirator was so small that changing atmospheric conditions could not have introduced any appreciable error in the measurement of the volume of the air.

In order to make certain that saturation really was reached in the saturating tube, the rate at which the air was passed over the salt was varied between comparatively wide limits, the maximum rate being not far from 4 liters per hour, the minimum rate about $\frac{1}{4}$ of this. Within these limits it was not possible to detect any certain difference in the results, so that it seems reasonably sure that equilibrium was really reached in the saturating tube and that the moisture was completely absorbed in the weighing tube.

Since in no case was the observed vapor pressure as high as that of water at the temperature of the room, condensation could not have occurred between the saturating and absorbing tubes. Obviously this condition limits the temperature at which the foregoing method may be used, unless the connection between the tubes is immersed in the thermostat. Such a modification has been successfully used in later experiments of the same nature.

Temperatures were determined to a few hundredths of a degree by comparison of the thermometers with accurate standards. The thermostats were thoroughly stirred and the temperature control by means of toluene regulators was as accurate as the thermometric readings. The thermostat at 0° was chilled by means of a layer of several inches of cracked ice. At 25°, an electric light bulb and on warm days a coil of cold water in addition served satisfactorily, while the bath was maintained at 50° by the method recently proposed by Derby¹ of passing a current through the water of the bath between carbon electrodes.

From the weight of water found in the absorbing tube was calculated its theoretical volume under standard conditions, upon the assumption that a mol occupies 22.41 liters. The volume of air in the aspirator was

¹ THIS JOURNAL, 35, 1767 (1913).

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TABLE I.
 $\text{H}_3\text{C}_7\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Temp °C	Wt of water, G	Volume of dry air at 0° and 760 mm Ct.	Rate per hour Liters	Average interior pressure Mm.	Aqueous pressure. Mm.
0	0.0028	7199	1.5	765.7	0.37
	0.0029	7231	1.5	765.0	0.38
	0.0027	7401	1.5	765.4	0.35
	0.0031	7303	1.6	764.5	0.40
					Av., 0.38
15	0.0081	7339	2.7	763.2	(1.03)
	0.0094	7582	2.8	764.2	1.18
	0.0094	7535	3.7	764.4	1.18
	0.0085	7292	3.6	764.6	1.10
	0.0092	7374	2.1	759.4	1.18
	0.0085	7130	2.0	759.4	1.12
					Av., 1.15
25	0.0198	7157	1.8	760.4	2.61
	0.0198	7070	1.7	761.4	2.64
	0.0200	7098	1.4	761.0	2.66
	0.0199	7016	1.6	760.4	2.67
	0.0199	6903	2.9	755.1	2.70
	0.0197	7066	1.0	762.7	2.64
					Av., 2.65
40	0.0627	7352	2.2	743.4	7.80
	0.0614	7216	2.5	743.2	7.78
	0.0629	7336	2.4	742.3	7.83
	0.0610	7220	2.2	742.5	7.72
	0.0634	7415	2.6	742.2	7.81
	0.0621	7285	2.0	743.0	7.80
					Av., 7.79
50	0.1228	7396	2.7	764.0	15.47
	0.1190	7172	1.8	764.9	15.47
	0.1262	7483	1.6	761.9	15.66
	0.1223	7246	1.5	762.3	15.68
	0.1178	7175	1.1	761.4	(15.24)
	0.1231	7379	2.6	759.5	15.44
	0.1192	7147	2.7	759.4	15.43
	0.1254	7491	1.2	761.1	15.53
	0.1216	7247	1.3	761.6	15.57
	0.1257	7501	2.1	761.0	15.54
	0.1221	7271	2.1	761.2	15.57
	0.1231	7352	1.6	766.6	15.64
					Av., 15.55
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.					
0	0.0088	6993	1.6	763.7	1.20
	0.0092	6866	1.7	764.2	1.27
	0.0094	7241	2.0	762.8	1.24
	0.0092	7135	2.0	763.3	1.22

TABLE I (continued).

Temp. °C.	Wt. of water G.	Volume of dry air at 0° and 760 mm. Cc.	Rate per hour. Liters	Average interior pressure. Mm.	Aqueous pressure. Mm.
	0.0092	6609	2.7	761.1	1.31
	0.0096	7307	2.4	750.0	1.19
	0.0094	7383	2.7	749.7	1.19
	0.0097	7330	2.8	744.6	1.22
	0.0095	7200	2.3	744.6	1.22
					Av., 1.23
15	0.0327	7501	2.4	765.0	4.13
	0.0313	7230	1.9	764.7	4.10
	0.0322	7455	2.8	764.6	4.09
	0.0303	7201	2.2	764.2	3.98
	0.0317	7414	2.8	763.4	4.04
	0.0297	7170	2.7	762.4	3.91
	0.0321	7298	2.6	746.0	4.06
	0.0311	7133	2.5	745.3	4.02
	0.0315	7374	2.6	745.5	3.94
	0.0306	7202	2.0	745.7	3.92
	0.0316	7304	2.8	744.3	3.98
	0.0303	7186	2.7	744.0	3.88
	0.0317	7320	2.4	748.6	3.91
	0.0309	7384	2.5	748.4	3.88
					Av., 3.99
25	0.0642	6988	1.6	757.7	8.56
	0.0634	7038	2.3	756.0	8.39
	0.0638	7157	1.4	762.9	8.37
	0.0622	7115	1.2	760.6	8.18
	0.0626	7020	1.4	760.2	8.34
	0.0643	7205	1.7	764.6	8.39
	0.0631	7108	1.6	765.1	8.36
	0.0653	7272	1.7	762.1	8.42
	0.0649	7198	2.0	762.2	8.45
	0.0643	7443	1.6	761.8	8.32
	0.0654	7405	1.5	767.1	8.34
					Av., 8.37
		<chem>Na2SO4 10H2O</chem>			
0	0.0213	7340	1.6	765.0	2.75
	0.0208	7082	2.2	765.1	2.78
	0.0209	7166	2.4	764.6	2.76
	0.0204	6912	1.6	759.8	2.78
5	0.0208	7088	1.6	759.5	2.76
					Av., 2.77
15	0.0714	7268	2.3	764.3	9.23
	0.0721	7359	2.3	764.7	9.21
	0.0745	7595	2.8	763.7	9.21
	0.0718	7146	3.1	764.3	9.18
					Av., 9.21

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TABLE I (continued).

Temp ° C.	Wt of water G	Volume of dry air at 0° and 760 mm. Cc	Rate per hour Liters	Average interior pressure Mm	Aqueous pressure Mm
25	0 1506	7224	1 6	760 8	19 23
	0 1488	7114	2 0	760 9	19 30
	0 1442	6916	2 6	759 1	19 19
	0 1475	7106	1 2	7 1 5	19 17
	0 1457	7006	1 3	761 9	19 21
	0 1490	7191	1 6	761 1	19 13
	0 1517	7299	1 "	761 1	19 18
	0 1497	7208	1 6	761 2	19 17
					Av, 19 20

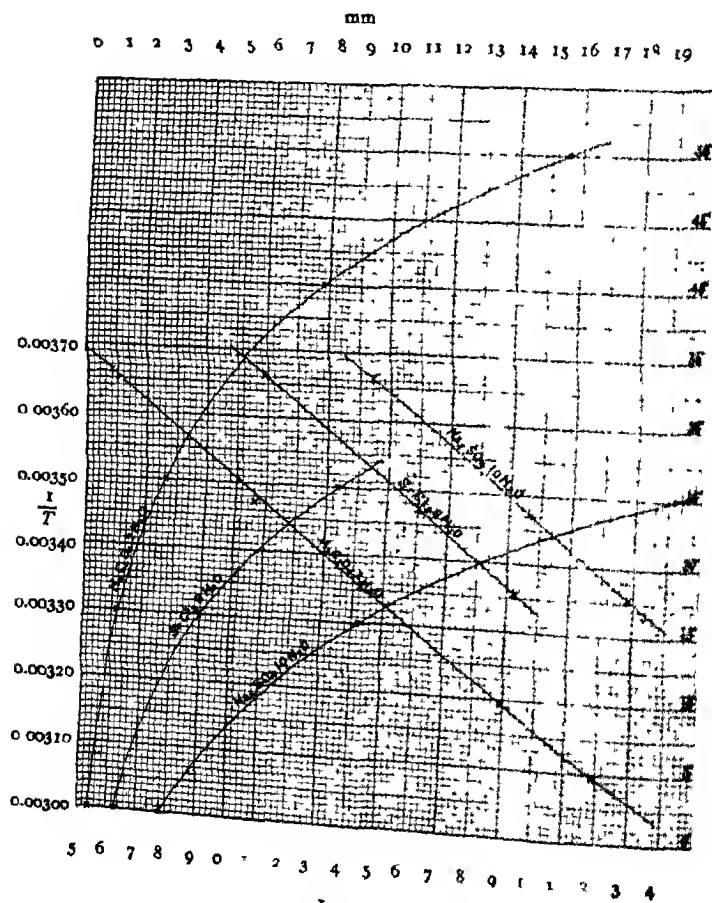


TABLE II.
 $H_2C_2O_4 \cdot 2H_2O$.

Temp	Observed. Mm.	Calculated. Mm.	Difference. Mm.
-25°	...	0.05	..
-15	..	0.11	..
0	0.38	0.38	0.00
15	1.15	1.24	+0.09
25	2.65	2.65	0.00
40	7.79	7.80	+0.01
50	15.55	15.56	0.0
60	.	30.34	..
70	.	57.95	..

 $SrCl_2 \cdot 6H_2O$.^a

-25°		0.14	..
-15		0.35	..
0	1.23	1.23	0.00
15	3.99	3.99	0.00
25	8.37	8.37	0.00
40		23.99	..
50		46.56	..

 $Na_2SO_4 \cdot 10H_2O$.^b

-25°		0.27	..
-15		0.72	..
0	2.77	2.77	0.00
15	9.21	9.21	0.00
25	19.20	19.19	-0.01
40	.	52.97	..
50		98.85	..

^a Frowein, *Z. physik. Chem.*, 1, 5 (1887)

Temperature	Mm
14.75°	3.29
20.34	5.14
25.06	7.82
30.01	10.87
34.66	15.33
39.45	21.57

 Andreae, *ibid.*, 7, 260 (1891).

19.7°	5.61
25.6	8.72
29.9	11.84
34.1	15.83
37.55	19.86

^b Lescœur, *Ann. chim. phys.*, [6] 21, 329 (1890)

0°	3.8
5	5.2
10	7.0
15	9.7
20	13.9
25	19.0
29	24.0

corrected to the same conditions, after allowing for a slight difference in pressure inside and outside the aspirator, determined with an open-arm water manometer attached to the aspirator bottle. The volume of the water vapor, divided by the volume of dry air plus the volume of the water vapor, and multiplied by the total interior pressure, yields the aqueous pressure of the salt under the conditions of the experiment. The results are given in the tables.

On the accompanying curves the aqueous pressure is plotted against the temperature, and the logarithm of the aqueous pressure is plotted against the reciprocal of the absolute temperature. In the latter case the points lie very nearly upon straight lines, almost exactly so with sodium sulfate. These lines are represented very closely by the following equations:¹

$$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \quad \log p = 18.053 - \frac{9661}{T + 250}$$

$$\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \quad \log p = 15.081 - \frac{6371}{T + 152}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \quad \log p = 10.566 - \frac{2794}{T + 3}$$

In Table II the observed values are compared with those calculated from the equations. The concordance is such as to inspire confidence in results obtained by extrapolation over a moderate temperature range.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF BRISTOL.]

COLLOIDAL ELECTROLYTES. SOAP SOLUTIONS AND THEIR CONSTITUTION.²

BY JAMES W. MCBAIN AND C. S. SALMON

Received June 11, 1918

Colloidal electrolytes are salts in which an ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity just as well or even better than the simple ion it replaces. This is the conclusion to which our 6 years study of soap solutions has led us

¹ Antome, *Compt rend.*, 110, 632 (1890); $\log P = A + \frac{B}{T + C}$

² This is the paper referred to by McBain, *Trans. Faraday Soc.*, 9, 99 (1913); *Kolloid-Z.*, 13, 56 (1913), and *Trans. Chem. Soc.*, 105, 957 (1914), whose publication has been delayed owing to the outbreak of war. The work was completed in the early Summer of 1914. Previous papers from this laboratory on the constitution of soap solutions commence with McBain and Taylor, *Ber.*, 43, 321 (1910), *Z. physik. Chem.*, 76, 179; (1912), further papers, *Trans. Chem. Soc.*, 99, 191 (1911), *Z. physik. Chem.*, 99, 191 (1911); 101, 2042 (1912); 105, 417, 957 (1914), *Trans. Faraday Soc.*, 9, 99 (1913); *Kolloid-Z.*, 12, 256 (1913)

This newly recognized class will probably prove to include, under certain conditions, most organic substances containing more than 8 carbon atoms capable of splitting off an ion of any kind, such as acid and alkali proteins, dyes, indicators, sulfonic acids and sulfonates, soaps, etc. Probably our conception of such inorganic substances as certain salts of the heavy metals, for instance chromium chloride, sodium tungstate or zincate, and certainly such substances as sodium silicate, will have to be revized in the light of this new knowledge. Many non-aqueous solutions also are comprized in this category, as will be shown elsewhere. Indeed it is probable that this new class contains as many members as all acids and bases put together.

In a measure the properties of this ionic micelle must apply to all colloids which possess even slight electrical charges. In the cases of proteins and soaps at high concentration, the undissociated substance is an ordinary colloid while the organic ion is a micelle. In dilute soap solutions, on the other hand, the undissociated molecules possess only the simple stöchiometric weight and the ions too are simple.

As the previous papers are somewhat scattered and as the data described in this paper derive their significance from combination with the previous work, a brief résumé is necessary.

When McBain and Taylor, in 1908, planned their attack on this subject, they chose soap as the material for their experiments because of the relative simplicity of its components, and also on account of its industrial importance. McBain had already shown that quite complicated cases, such as solutions of cadmium iodide, could be readily interpreted within the limits of the dissociation theory.¹ Here, however, they found a case which necessitated an extension of that theory. They recognized the importance of the conclusions towards which their results led, and decided deliberately not to adopt the explanation just outlined, as long as it was possible to maintain any other. Further, the methods of investigation were to be only the powerful incontestible ones which had served to establish the theory of solutions and of electrolytes. Viscosity measurements, for instance, and other colloidal methods were rejected as being in the nature of circumstantial evidence only.

At that time Krafft's work on the subject was universally accepted, and it was believed that soap was just an ordinary colloid. Kahlenberg and Schreiner's measurements of the conductivity of certain dilute soap solutions were simply explained away as being due to impurities, hydrolysis and dilution.

McBain and Taylor² spent several years in measuring the conductivity of sodium palmitate solutions of all concentrations, near the boiling

¹ *Z. Elektrochem.*, 11, 222 (1908); *THIS JOURNAL*, 34, 1134 (1912).

² *Z. physik. Chem.*, 76, 179-209 (1911).

point, as Krafft's molecular weight measurements had been made at this temperature, and as the concentrated solutions were not liquid at low temperatures. They found a high conductivity in all solutions.¹ This showed conclusively that soap solutions consist to a large extent of something other than a neutral colloid. The next step was to show by two quite independent methods, namely by the rate of catalysis and the electromotive force of the hydrogen² electrode, that the hydroxyl ion present was negligible, its concentration being only about 0.001 *N*. Hence the high conductivity was necessarily due to the soap itself.

The present paper shows again³ that Krafft's well known work is completely erroneous, and it describes measurements of the osmotic pressure of numerous soap solutions by a vapor tension method, showing that in extreme cases the sole constituent that is not a colloid is the sodium or potassium ion, although this is present in high concentration and must, therefore, be counterbalanced by a colloidal micelle of high equally opposite charge and conductivity. Other related work, to the same effect, on the freezing points of some potassium soap solutions is being described elsewhere.

No less remarkable is the demonstration that as the solutions become more dilute a gradual transition from colloid to crystalloid takes place, until in dilute solutions the soap is essentially an electrolyte just like potassium acetate. This refers to the undissociated colloid as well as to the colloidal ion or ionic micelle. In every solution again there is established a perfectly definite, completely reproducible equilibrium between all these constituents, both colloids and crystalloids.

The Experimental Method.

McBain and Taylor⁴ have shown the impossibility of using the ordinary boiling-point method with these solutions, owing to the presence of a large amount of air which does not escape from the bubbles and, therefore, by its partial pressure, wholly invalidates the results. Krafft's observation that soap solutions boil just above or below the boiling point of water, although perfectly correct, is thereby wholly deprived of significance. The same consideration renders illusory the apparent vapor pressure as measured by Smits in an ordinary tensimeter. McBain and Taylor⁴ were able to obtain direct confirmation of this by experiments which in one case extended over 3 weeks, where most of the air was eliminated and a vapor tension in agreement with that obtained here was finally observed.

¹ Subsequent measurements of conductivity of various soaps solution from this laboratory: *Trans. Chem. Soc.*, 99, 191 (1911); 101, 2042 (1912); 103, 417 (1914).

² *Trans. Chem. Soc.*, 103, 957-977 (1914); rate measurements not yet published, completed in 1914.

³ See McBain and Taylor, *loc. cit.*, pp. 185-186.

⁴ *Loc. cit.*

The present experimental results consist of measurements of the rise of the boiling point or lowering of the vapor pressure of soap solutions as measured by Cummings'¹ dew-point method suitably modified. The experiments cover an extraordinary range of concentration from very dilute solutions up to practically anhydrous solids. It is a matter of indifference when using this method whether the system studied is liquid or solid, viscous or limpid, one phase or several phases. The results are accurate to 0.01° . For instance, the vapor pressures of a number of soap solutions were measured by one of us (J. W. M.) and subsequently the other carried out the same series of measurements without being aware of this. Our results agreed either to 0.00° or 0.01° in every case. This degree of accuracy was made possible through a special treatment of the silver surface described below.

Fig. 1 shows a diagram in cross-section of the apparatus employed. A highly polished silver tube with silver bottom was closed with a cork at the top. Through the cork were inserted a thermometer and 2 tubes through which a rapid current of water was circulated by a power pump from and to a thermostat of adjustable temperature. The silver tube was held in a cork in a glass vessel which contained the solution to be studied. The top of the glass

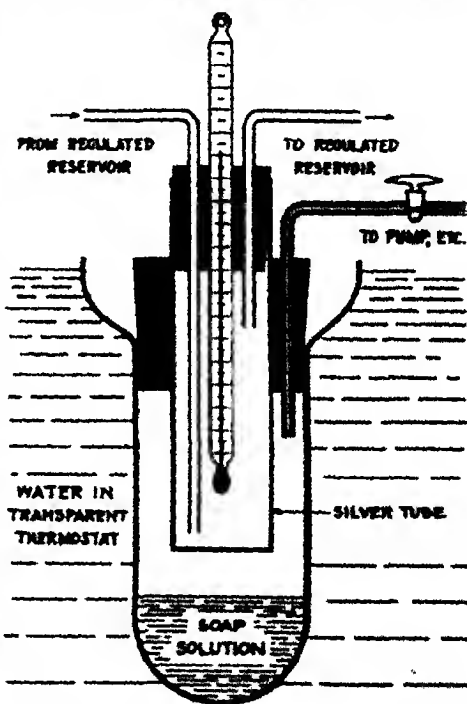


Fig. 1.

vessel rose an inch or so above the cork so that the closed space was completely immersed in the water of a thermostat which had glass sides. Further, a capillary glass tube passed through the cork holding the silver tube and could be connected with an air pump and thus evacuated or the pressure adjusted to any desired value. This tube was closed by a glass tap.

The following device alone rendered possible the attainment of accurate results. The silver tube was kept most highly polished; but as it was

¹ *Trans. Chem. Soc.*, 95, 1772 (1909).

extremely difficult to detect the first very slight dimming of the silver surface, a definite portion of the silver surface was so treated that no dew deposited on it, so that it therefore remained bright and afforded by juxtaposition a contrast with a slightly clouded surface. The test of the appearance or disappearance of the dew was then the first appearance of this sharp boundary or the attainment of perfect uniformity of the surface. To produce this effect, boiling water was run through the silver tube and the bottom corner of the tube was dipped once into boiling conductivity water. The water evaporated at once but thereafter no dew would form on this part of the surface. In this way when the tube was subsequently viewed from the front the boundary line ran diagonally across the lowest part of the side of the tube. The attempt was made to extend this essential refinement of the dew-point method to various non-aqueous solutions, but without success. In every case dew formed all over the silver surface no matter how this had been treated or contaminated.

In making a determination, the main transparent thermostat is first adjusted to say 90.0° . It has to be filled with distilled water, stirring must be very vigorous, and the whole has to be carefully covered to prevent evaporation. For the same reason a large quantity of glycerine is added. The meniscus is kept at constant level by use of a constant level reservoir. The glass sides of the thermostat are kept carefully cleaned and polished for close observation. The adjustable auxiliary thermostat is filled with water covered by a deep layer of melted paraffin or is otherwise carefully protected.

The next step is to pass practically boiling water through the prepared silver tube and insert the latter into the glass vessel to about one cm. above the surface of the solution to be studied. This prevents first, condensing large amounts of water on the silver tube; second, altering the surface of the silver; third, dimming the glass when heavy dew is evaporated; and fourth, changing the concentration of the solution. The whole apparatus with the hot water passing through it is then inserted into the transparent thermostat as in Fig. 1. The holder is not rigid and it is, therefore, possible to shake the soap solution slightly and thus renew the surface if desired.

The glass tap is kept open for a few minutes to equalize pressure outside and inside, since the vapor pressure of the solution is considerable at this temperature. The tap is then kept closed. Owing to the high vapor pressure involved it was found quite unnecessary and inadvisable to evacuate the air in the apparatus. In later work water was often deliberately removed from the solution by this method and heavy dew could be instantly dissipated. On the other hand, the temperature dis-

turbance is very considerable. Thus for normal working with apparatus kept closed, the rather small amount of air present (say 200 mm. pressure) involved no appreciable lag in the diffusion of the water vapor (say 550 mm. pressure). Doubtless again, on account of this high vapor pressure, the use of the cork was quite without influence on the results.

The determination is now begun by very gradually lowering the temperature of the water running through the silver tube, carefully noting the temperature of the thermometer contained in it and also of the one in the thermostat with its bulb close to the solution. On the first sign of dew forming (slight discontinuity of the polished surface, the boundary line becoming faintly visible under bright and carefully adjusted illumination) the temperatures of both thermometers are read.

Immediately the supply of heat to the adjustable thermostat is altered to a value which will slowly raise the temperature of the running water. There is now a lag during which the dew increases, but soon it becomes faint and the silver surface is suddenly sensibly uniform. Both thermometers are again read, and the heat supply again diminished. Thus a long series of values for the appearance and disappearance of the dew is obtained. The temperature of the outside thermometer in the transparent thermostat is of course nearly or quite constant. The mean value for a series of at least 7 or 8 readings each way is quite reproducible by different experimenters working independently.

The apparent temperatures of appearance and disappearance of the dew differ on account of the lag referred to, but since pure water is measured similarly, the results for solvent and solution are strictly comparable. In this way the method resembles the ordinary Beckmann boiling-point method, where the absolute temperatures are always very inaccurate (perhaps by a degree or more) but where the difference in temperatures or rise in the boiling point is accurate to perhaps a few hundredths of a degree. Our dew-point results are about as accurate as an ordinary Beckmann determination in dilute solution, and the latter is wholly inapplicable to the cases here studied.¹ For moderate concentrations of substances such as sodium chloride they are several times more accurate. Thus, from the data given in the tables of Landolt and Börnstein, the dissociations indicated for 1.0 *N* solution of potassium and sodium chlorides are 80 and 94%, respectively, whereas our method gives 78 and 76%, respectively, in agreement with our results for the corresponding acetates, namely, 78 and 74%.

A typical experiment showing only a few readings is quoted below, Table I:

¹ McBain and Taylor, *loc. cit.*

TABLE I.
Dew Point of 1.0 *N* Potassium Stearate at 90°.

Silver tube thermometer. ° C.	Thermostat thermometer ° C.	Temperature formation ° C.	Difference disappearance ° C.
89.43	90.00	(0.57)	
89.75	90.01		0.26
89.68	90.01	0.33	
89.75	90.00		0.26
89.68	90.00	0.32	
89.74	90.01		0.27
89.68	90.00	0.32	
89.75	90.01		0.26
89.69	90.00	0.31	
89.4	90.00		0.26
		Mean, 0.32	0.26
		Final mean, --0.29°	
		Thermometer error, --0.09°	

Hence the rise of boiling point due to the soap is 0.20° at 90° and the total concentration of all ions and molecules is 0.42 *N*.¹

Two other completely independent solutions measured on different occasions and involving 18 readings gave elevations of 0.20 and 0.205°.

The thermometric error was obtained by carrying out similar experiments with pure water. It consists essentially of the error in the calibration of the thermometer, but any personal error is eliminated at the same time. With water the difference in temperature between the appearance and disappearance of the dew was only from 0.01 to 0.03°, instead of the 0.06° difference between the temperatures in the final columns of the above table.

It will be noted that the first rough reading is usually neglected in taking the mean. An important practical point is a close inspection of the silver surface after the experiment, to see that it has remained quite clean.

The solutions were prepared in silver tubes from Kahlbaum's best chemicals, employing all the precautions described in previous communications. The weight of palmitic acid required to neutralize a known amount of sodium hydroxide in aqueous alcohol was only 0.1% smaller than the theoretical amount. Each concentration up to 1.5 *N* was prepared separately and at least in duplicate. Concentrations are given invariably in weight normality (number of gram equivalent weights of soap in 1000 g. of water).

Method of Calculating Dew-point Results.

When the silver tube is cooled just far enough to form a little dew the pure water thus formed is in equilibrium with its own vapor. The aqueous vapor pressure in the apparatus, therefore, can be ascertained by reference to the standard tables. But this vapor is also that which is exhi-

¹ It will be seen later that this is entirely due to the potassium ion.

bited by the soap solution present at the somewhat higher temperature of the thermostat. In other words, the difference in temperature between the silver tube and the soap solution is the rise in boiling point of water at reduced pressure due to the substance dissolved in it. The rise predicted for a 1.0 *N* solution of a crystalloid such as sugar, according to the familiar van't Hoff formula RT^2/s is 0.483° at 90° . Since the latent heat of vaporization of water is greater at lower temperatures, and T is less, this rise is slightly less than the rise of 0.5010° expected in the ordinary Beckmann method at 100° . The values of the constant taken for lower temperatures are: 70° , 0.414; 45° , 0.353; 25° , 0.303; 20° , 0.291°.

Results calculated by the related formula

$$\ln \frac{p}{p'} = \frac{n}{N}$$

gives a practically identical result. It is worth emphasizing both that these simple formulas are still approximately correct in surprisingly high concentrations, and that the osmotic effect is always somewhat greater than expected. Thus even in a 2.7 *N* solution of cane sugar containing about equal weights of water and cane sugar the error is still less than 12%.¹ The enhanced osmotic effect is generally accounted for by assuming hydration of the solute. Thus, in the case of cane sugar, the hydrate appears to contain 5 molecules of water to one of sugar. The point that is useful in the following is that the osmotic activity tends to be too great rather than too small.

Experimental Results and Deductions from Them.

I. *In concentrated soap solutions the only crystalloidal or electrolytic constituent is the potassium or sodium ion.*—This means that nearly half of the current is carried by the negative colloid, which must be as good a conductor as an ordinary ion. How this can be is explained later (see Section II).

For convenience, we shall discuss one particular example first, taking for this purpose the measurement of the 1.0 *N* potassium stearate solution recorded in Table I. This solution has at 90° an equivalent conductivity of 113.4 reciprocal ohms,² that of 1.0 *N* potassium acetate being 176.9 at the same temperature. It is evident that in this concentration the stearate conducts about $\frac{1}{3}$ as well as the acetate itself and that it must, therefore, be recognized as an excellent conductor.

We now pass to the quantitative evaluation of these conductivity data in order to arrive at the concentration of the potassium ion present.

If the negative ion were an ion at all, the high molecular weight of the stearate radical would lead us to predict that the stearate ion would not

¹ *Trans. Faraday Soc.*, 11, 39 (1915).

² *Trans. Chem. Soc.*, 105, 424 (1914).

conduct as well as the acetate ion (116 reciprocal ohms at 90°). In accordance with the extensive knowledge we possess of the dependence of mobility upon molecular weight and chemical constitution we should predict for the stearate ion a mobility at 90° of about 90 reciprocal ohms. This, with a mobility of 188 reciprocal ohms for the potassium ion, would make the conductivity of potassium stearate 278 for complete dissociation.

Using this result, the concentration of potassium ion is found to be $\frac{113}{278} \times 1.0 N = 0.41 N$. This equals the observed total concentration of crystalloidal constituents, 0.42 *N*, within the experimental error. Hence everything else, that is, the whole of the stearate, including whatever carries the equivalent of this large amount of electricity, must be colloid and not simple unpolymerized stearate of any sort.

II. *These highly mobile ionic micelles may be plausibly predicted or explained on mechanical grounds.*—The conception of these highly mobile heavily hydrated micelle, outlined above, was originated by McBain in a general discussion on colloids and viscosity held by the Faraday Society in 1913.² It was put forward to remove one of the chief difficulties in interpreting the properties of acid and alkali albumens, since it reconciles their enormous viscosity with their quite good conductivity.

Stokes' law applied to a sphere of radius *a* moving through a liquid of viscosity η may be expressed as follows: $V = \frac{E}{6\pi\eta a}$, where *V* is the velocity caused by the action of a force *F*. Perrin and others have shown that this law applies to colloidal particles. In conductivity experiments the force *F* is due to the electric charge on the ion which is 96540 coulombs per gram ion. If this charge could be varied without other alteration of the ion, the driving force, velocity, and mobility or conductivity would vary in direct proportion.

If, on the other hand, a number of ions, say a dozen, were to coalesce, the resulting particles would be driven by a force equal to 12*F*. The velocity would not be proportionally great, for the radius of the sphere would now be increased by $a^{12/12} = 2.3a$. The new velocity, therefore, would be $12/2.3 = 5.2V$. This 5-fold increase in mobility of the aggregate as compared with the separate ions would in practice be counterbalanced by the effect of the greatly enhanced electrostatic potential of the aggregate in attracting water molecules and other material, so that such an aggregate would become a heavily hydrated micelle. This great hydration would usually more than offset the extra mobility expected, and the results would be a colloidal particle of somewhat less mobility than a rather slow true ion. The hydration accounts for the enormous

¹ *Trans. Chem. Soc.*, 105, 423 (1914).

² *Trans. Faraday Soc.*, 9, 99 (1913), *Kolloid-Z.*, 23, 56 (1913)

mechanical viscosity observed in all the systems mentioned and also for its variation with the concentration of the constituents, etc. Such hydration has been commonly deduced by workers in this field for other reasons.

What is essentially new in the conception of a mobile micelle here presented, is the mechanism by which the micelle is built up round an aggregate of simple stearate ions which still retain their original electrical charges. In the study of such electrolytic colloids as the proteins it has long been assumed that an ion could be colloidal or associated with colloidal matter, but that was chiefly because quite enormous values are taken for the molecular weights of proteins, and molecules of such bulk must be expected to behave like colloids. Only a relatively low conductivity has ever been ascribed to them.¹

III. *In dilute solutions on the contrary the colloid breaks up into simple ions and simple undissociated soap.*—On account of the limitations of the dew-point method in dilute solutions 0.2 *N* soap solutions were the most dilute measured. The result of measurements of potassium palmitate solutions of this concentration at 90° was as follows: Lowering of dew point = rise of boiling point at 90° = 0.12°. Hence total concentrations of all ions and molecules present = 0.25 *N*. Now the molar conductivity of 0.2 *N* potassium palmitate at 90° is 111.0 reciprocal ohms.² If the conductivity at infinite dilution is 304, the concentration of potassium ions is 0.072 *N*; if it be 278, the concentration is 0.080 *N*. Hydrolysis does not affect this result by more than about 2%,³ and this may be neglected for our present purpose.

Taking the second result, $K = 0.080$ *N*, the concentration of total crystalloids present being 0.25 *N*, leaves a concentration of $0.25 - 0.08 = 0.17$ *N* for crystalloids other than the potassium ion. The total undissociated soap is $0.200 - 0.080 = 0.120$ *N*. Thus, even if all the undissociated soap here is in simple crystalloidal form there is still a $0.17 - 0.12 = 0.05$ *N* concentration of crystalloid to account for, and this must be afforded by simple palmitate ions, since the hydroxyl ions have been shown to be only about 0.01 *N*. The small balance of 0.03 is all that can be colloid.

Whether this relatively small amount of colloid is due to remaining

¹ It is a well known and striking fact that many mechanical suspensions as well as colloidal particles have an actual mobility in the electrical field comparable with that of an ion. This has not, however, been associated with high conductance, for it has been generally explained on the Helmholtz conception of the shearing of an electrical double layer, water upon water, not on the possession of such high electrical charge as we are here forced to recognize. Thus high mobility has not meant high conductivity although both must be attributed to an ionic micelle.

² *Trans. Chem. Soc.*, 105, 428 (1914).

³ *Ibid.*, 105, 966 (1914). Confirmed by unpublished measurements of catalysis.

nitrate or to neutral colloid will be discussed below. The point to notice is that not more than a quarter of the undissociated palmitate, nor more than $\frac{1}{2}$ of the palmitate ion can be in colloidal form. If there be some of each in colloidal form this amount has to be divided up between them so as not to exceed a total of 0.03 *N*.

It is quite clear that in 0.2 *N* palmitate solution the break-down of the colloid has gone moderately far, and that further dilution would rapidly complete it. In other words, we have a clear case of transition from colloid to crystalloid in the same solution, depending only on the concentration, and forming a true, stable, reversible equilibrium in each concentration. That a colloid can thus enter into true equilibria would appear to be of great importance for the theory of colloids.

IV. "Molecular weights" of typical solutions of potassium and sodium salts of fatty acids at 90°.—Before further discussion a body of data may be presented for 77 typical potassium and sodium soap solutions giving the final results of measurements of the dew point carried out as described above. Almost every number in Table II and Table III is the mean of several such tables as Table I, carried out on independent solutions. Further results for concentrated solutions and other cases are given later. The total work done so far involves several thousand individual readings.

TABLE II.
Rise of Boiling Point at 90° for Potassium Salts.

Weight normality.	Stearate, C_{18} °C	Palmitate, C_{16} °C	Myristate, C_{14} °C	Laurate, C_{12} °C	Decoate caprate, C_{10} °C	Octoate caprylate, C_8 °C	Hexoate caproate, C_6 °C	Acetate, C_2 °C
0.2	0.10	0.12	0.13	0.15	0.16	0.17	0.17	0.185
0.5	0.17	0.19	0.23	0.26	0.31	0.35	0.38	0.46
0.75	0.19	0.23	0.27	0.30	0.42	0.48	0.53	...
1.0	0.20	0.24	0.28	0.32	0.52	0.60	0.66	0.86
1.5	0.16	0.21	0.25	0.31	(0.65)			...
2.0	0.18	0.27	0.32	0.48	(0.72)			...
3.0	0.23			1.02				...

TABLE III
Rise of Boiling Point at 90° for Sodium Salts

Weight normality	Behenate, C_{20} °C	Stearate, C_{18} °C	Palmitate, C_{16} °C	Myristate, C_{14} °C	Laurate, C_{12} °C	Caprylate, C_8 °C	Acetate, C_2 °C	Any non-electrolyte by theory.
0.2	0.09	0.11	0.13	0.14	0.15	0.17		
0.5	0.11	0.18	0.20	0.24	0.28	0.37	0.45	0.10
0.75	...	0.22	0.24	0.28	0.32	0.50	...	0.24
1.0	0.09	0.23	0.25	0.29	0.34	0.62	0.84	0.36
1.5		0.18	0.22	0.27	0.33			0.48
2.0	0.11	0.19	0.50				...	0.72
3.0		0.30	1.23				...	0.97
								1.45

Tables IV and V give the total amounts of crystalloidal matter (ionized and otherwise), indicated by the data of Tables IV and V and expressed

in moles per 1000 g. of water. These are calculated as shown on page 435.

TABLE IV.

Total Crystalloidal Matter in Potassium Salt Solutions at 90°.

Mols per 1000 g. of Water.

Weight normality.	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Caprate, C_{10}	Caprylate, C_8	Caproate, C_6	Acetate, C_2
0.2	0.21	0.25	0.27	0.31	0.33	0.35	0.35	0.38
0.5	0.35	0.39	0.48	0.54	0.64	0.72	0.79	0.95
0.75	0.39	0.48	0.56	0.62	0.87	0.99	1.10	...
1.0	0.42	0.50	0.58	0.66	1.08	1.24	1.37	1.78
1.5	0.33	0.44	0.52	0.64	1.35
2.0	0.37	0.56	0.66	0.99	1.50
3.0	0.48	2.11

TABLE V.

Total Crystalloidal Matter in Sodium Salt Solutions at 90°.

Mols per 1000 g. of Water.

Weight normality.	Behenate, C_{22}	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Caprylate, C_8	Acetate, C_2
0.2	0.19	0.23	0.27	0.29	0.33	0.35
0.5	0.23	0.37	0.41	0.50	0.58	0.77	0.93
0.75	0.46	0.50	0.58	0.66	1.04
1.0	0.19	0.48	0.52	0.60	0.70	1.28	1.74
1.5	0.37	0.46	0.56	0.68
2.0	0.23	0.39	1.04
3.0	..	0.62	2.55

Far better than any further discussion of the reliability and reproducibility of these independent measurements is a glance at a graph of the results. Fig. 2 presents the directly observed dew-point lowerings plotted against the dilution¹ in liters as abscissas. The curves for the sodium soaps are only dotted in, for convenience of comparison. It is evident that the salts fall into two classes. From the acetate up to the caprate (C_{10}) the curves are regular, showing dissociation, although in the more concentrated caprate solutions the lowering only slightly exceeds that of an ordinary non-electrolyte. On the other hand, from the laurate (C_{12}) upwards, each curve passes through a pronounced maximum lowering at about 1.0 N ² and a definite minimum lowering again at 1.5 N . Above these concentrations the lowering rapidly increases again.

It is worth while remembering that the stearate above 1.5 N is hardly a solution; 1.5 N sodium stearate at 90° is a viscid gum. On the other hand, 2.0 N potassium laurate solution with a similarly shaped curve, is a clear oily liquid. The form of the curve is thus definitely due to the constituents in solution, not to mechanical effects such as formation of

¹ The concentrations are in grams per kg.

² The exact concentration is slightly higher than 1.0 N for the lower members, and slightly lower than 1.0 N for the behenate. This agrees with the previous work on conductivity published from this laboratory (*Trans. Chem. Soc.*, 105, 435 (1914)).

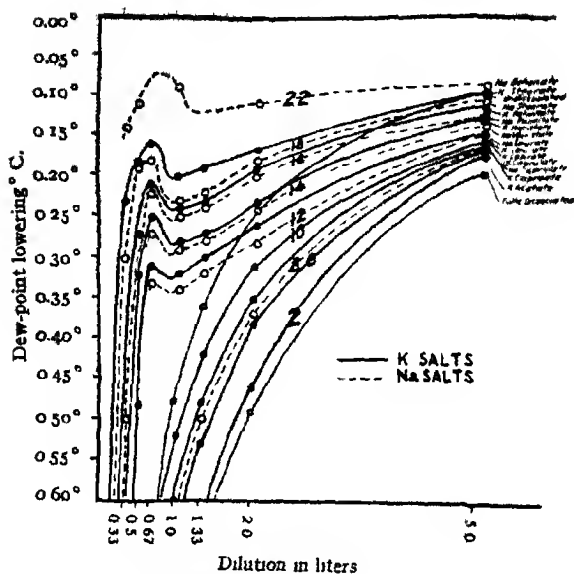


Fig. 2.—Dew-point lowerings of potassium and sodium salts of fatty acids at 90°

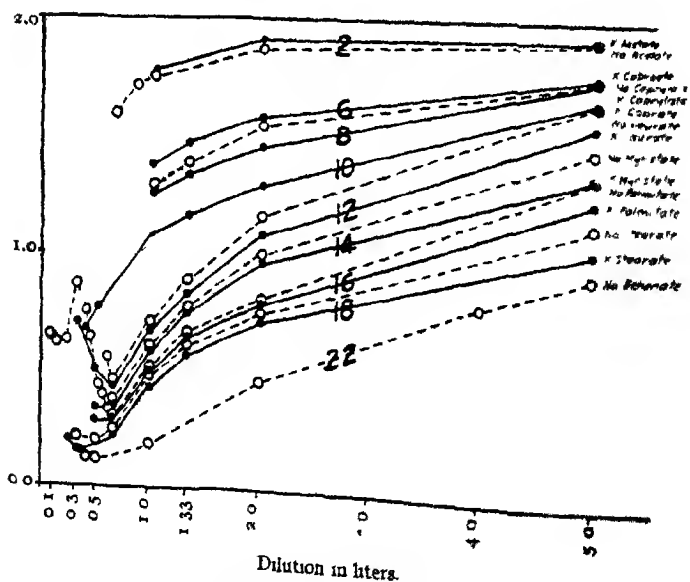


Fig. 3.—Osmotic activity

gel or change of state. The effect is also not due to hysteresis, as is the case in the dehydration of certain gels, for it is independent of the age or method of preparation of the soap solution or whether water may have been previously added or taken away.

Fig. 3 presents the results in a wholly different form. Here the ratios of the lowerings to that predicted for the same concentration of any non-electrolyte, in other words van't Hoff's factor i , are plotted against the dilution in liters. The curves for the sodium salts are dotted as before. The significance of these results is that they give directly, for each concentration, the proportion of total crystalloids present, relative to that in the case of a non-electrolyte which is taken as unity, that of a completely dissociated binary electrolyte being 2.

It will be noted that the present consideration differs from the crude treatment almost invariably accorded to osmotic data whether in aqueous or non-aqueous solution, where the data are simply scanned for evidence of association or dissociation. The usual interpretation would be to jump to the conclusion that a 0.20 N potassium stearate or a 0.5 N sodium myristate, for example, consists of simple undissociated molecules, a result which is of course irreconcilable with the conductivity, as in the case of many non-aqueous solutions. Similarly, a normal solution of sodium or potassium palmitate would be regarded as being composed of undissociated double molecules, again irreconcilable with the high conductivity. It will be seen how the method developed under Sections I and III will probably clear up many otherwise unexplained anomalies in non-aqueous solutions where such cases constantly occur.

The results cover a very wide range, from the ordinary highly dissociated electrolytes represented by the acetates, to the concentrated solutions of the behenate (C_{22}) where the total amount of crystalloid, ionized and non-ionized, is only a tenth of the total concentration. The data for the behenate will be discussed in a separate communication in conjunction with other data.

It is quite striking with what regularity the phenomena set in. The transition from any one type to the other is quite gradual as we ascend the homologous series. Again, the curves for each fatty acid run in pairs for the sodium and potassium salts. Only in concentrations above 1.5 N do the potassium and sodium soaps diverge appreciably, although in every case the potassium salt solution contains slightly more colloid. This last result had been already deduced from our study of conductivity.¹

V. In 1.0 N solutions at 90° the total colloid present equals at least 15% in the case of the hexoate, increasing to nearly the whole in the cases of the

¹ *Trans. Chem. Soc.*, 105, 425 (1914).

higher soaps, but falling off rapidly on dilution—We have now in Tables IV and V the total amount of crystalloid in each solution (K^+ or Na^+ , simple soap ion such as palmitate ion P^+ , as simple undissociated neutral soap such as NaP). Next come the results of the conductivity measurements which give the concentrations of the potassium or sodium ions, (Tables VI and VII). The values taken for the mobilities of the negative radicals are, behenate to laurate 90, caprate 92, caprylate 94, caproate 98, acetate 116, also sodium 139 and potassium 188 (See page 434 and also below.¹)

TABLE VI

Concentrations of Potassium Ion in Salts at 90°

Weight normality	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Caprate, C_{10}	Caprylate, C_8	Caproate, C_6	Acetate, C_2
0.2	0.072	0.080	0.094	0.103	0.135	0.135	0.140	0.145
0.5	0.205	0.202	0.243	0.262	0.278	0.298	0.310	0.324
0.75	0.305	0.345	0.366	0.384	0.399	0.380	0.426	0.454
1.0	0.408	0.446	0.489	0.515	0.521	0.527	0.523	0.582
1.5				0.696		0.726		0.800
2.0				0.885		0.898		1.01

TABLE VII

Concentrations of Sodium Ion in Salts at 90°

Weight normality	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Acetate, C_2
0.2	0.053	0.079	0.085	0.099	0.140
0.5	0.166	0.195	0.216	0.239	0.303
0.75	0.272	0.286	0.324	0.350	0.409
1.0	0.386	0.369	0.405	0.455	0.512
1.5	0.553	0.553	0.543	0.615	0.664

By subtracting corresponding values in Tables VI and VII from those in Tables IV and V, we arrive at the values in Tables VIII and IX, which give all crystalloidal constituents other than potassium or sodium ions. The remainder of the soap must, of course, be colloidal and the values for this are given in Tables X and XI.

TABLE VIII

Concentrations of Crystalloidal Constituents other than K^+ at 90°

Weight normality	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Caprate, C_{10}	Caprylate, C_8	Caproate, C_6	Acetate, C_2
0.2	0.14	0.17	0.18	0.21	0.20	0.22	0.21	0.24
0.5	0.15	0.19	0.23	0.28	0.36	0.43	0.43	0.63
0.75	0.08	0.11	0.19	0.24	0.47	0.58	0.67	
1.0	0.01	0.05	0.09	0.15	0.56	0.72	0.85	1.20
1.5				0.05				
2.0				0.11				

¹ Direct determinations of these values were being carried out in this laboratory in the early summer of 1914. It is hoped ultimately to complete them.

TABLE IX.
Concentrations of Crystalloidal Constituents other than Na^+ at 90° .

Weight normality	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Acetate, C_2
0.2	0.18	0.19	0.20	0.23	...
0.5	0.20	0.22	0.28	0.34	0.63
0.75	0.18	0.1	0.26	0.31	...
1.0	0.09	0.15	0.20	0.25	1.23
1.5	—0.20	—0.11	0.02	0.07	.

TABLE X.
Concentrations of Total Colloid in Potassium Salt Solutions at 90° .

Weight normality	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Caprate, C_{10}	Caprylate, C_8	Caproate, C_6	Acetate, C_2
0.2	0.06	0.03	0.02	—0.01	0.00	—0.02	—0.01	—0.04
0.5	0.35	0.31	0.27	+0.22	0.14	+0.07	+0.02	—0.13
0.75	0.69	0.64	0.56	0.51	0.28	0.17	0.08	.
1.0	0.99	0.95	0.91	0.85	0.44	0.28	0.15	—0.20
1.5	.	.	.	1.55
2.0	.	.	.	1.89

TABLE XI.
Concentrations of Total Colloid in Sodium Salt Solutions at 90° .

Weight normality	Stearate, C_{18}	Palmitate, C_{16}	Myristate, C_{14}	Laurate, C_{12}	Acetate, C_2
0.2	0.02	0.01	0.00	—0.03	...
0.5	0.30	0.28	0.22	+0.16	—0.13
0.75	0.57	0.54	0.49	0.44	..
1.0	0.91	0.85	0.80	0.75	—0.23
1.5	(1.70)	1.61	1.48	1.43	...

It is necessary to pause again to consider the validity of this comparison of osmotic with conductivity data. It is undoubtedly the case that the osmotic values are too high, presumably, as already mentioned, on account of hydration of the solute. The ebullioscopic method shows this particularly, for Beckmann, by this method, obtained values from sodium acetate corresponding to dissociations which actually increased from 78% in 0.25 *N* solution to 95% in 1.9 *N* solution. The apparent dissociations of potassium and sodium chlorides pass through minima of 76 and 84% at about 0.1 *N*, rising to 89% for 2.5 *N* potassium chloride and the impossible value of 106% for 2.1 *N* sodium chloride.

The dew-point method is much more reliable than the ebullioscopic method since the latter measures only a very rough dynamic thermal equilibrium instead of a true static one. But even so, the dissociation deduced for sodium acetate from the conductivity falls short of the osmotic activity by 20 to 23%. Even were this all due to hydration, 7 or 8 molecules of water would have combined with the acetate and its ions, a not improbable result in the light of other evidence.

On the other hand, the results of conductivity measurements are definitely too low, on account of the retarding influences of viscosity on the

mobility of ions. The form which the viscosity correction should take is still a matter of speculation¹ but it follows from the present paper that those in use are not universally correct. For example, the solutions often have their observed conductivities corrected directly by multiplying these values by the ratio between the viscosities of solvent and solution, more usually a fractional power of this ratio is employed. The former is certainly the correction required by Stokes' Law. But in some of the soap solutions here discussed the viscosity is 1000 times greater than that of water, and it is very obvious that the high observed conductivity cannot be increased even a few fold without exceeding 100% dissociation. The viscosity correction ought certainly to be made in all solutions, but it is evident that its exact formulation has still to be ascertained. Even in viscous soap solutions the correction cannot be very large. It may be legitimate to take the viscosity of the solution itself in a molecular, homogeneous, crystalline solution, but it must be that of the intramolecular liquid in the case of a colloidal electrolyte.

In the case of the acetates here measured the viscosities of 1.0 *N* solutions of potassium and sodium acetates at 18° and 25° exceed that of water by 26 and 39%, respectively. Although this would be somewhat less at 90°, it is ample to account for any divergence between the conductivity and osmotic effect, but probably both viscosity and hydration each contribute a share.

We have seen then that the osmotic activity is certainly too great, and that conductivity data are certainly too small. And yet in concentrated solutions of the higher soaps the osmotic effect is not enough even for the sodium and potassium ions alone as deduced from the conductivity. This is satisfactory in establishing the main thesis of this paper.

However, looking at Tables X and XI, we see that 1.5 *N* solutions of potassium laurate, sodium stearate and sodium palmitate give more colloid than is possible when calculated by taking the conductivity and dew point without correction. The permissible correction as just discussed would operate in the wrong direction. The obvious course is to admit that the basis of the calculation of the concentration of the sodium and potassium ions in concentrated solutions is incorrect, in that the ionic micelle (it cannot be the potassium ion) has a mobility even higher than that assumed above 90 mhos at 90°.

To reconcile the data for 1.5 *N* sodium stearate it is necessary to assume for the micelle a mobility at least as great as that of potassium ion (188 mhos). This could easily be effected through diminishing hydration of the micelle in concentrated solution according to the data of Section II. Other evidence in support of this plausible assumption will be discussed below. (See Section XIV.)

¹ Cf. *Trans. Chem. Soc.* 102, 111 (1922).

The only alternative would appear to be the assumption of a positive as well as a negative micelle, to replace some of the potassium ion. However, it is not in accordance with what we know of the behavior of colloids that two oppositely charged colloids should be simultaneously present in a solution.¹

On the whole then, the tables presented appear to be substantially correct for all dilute solutions, and in every case in Tables X and XI to indicate minimum values for the amounts of colloid present.

The first point to notice is that every 0.1 *N* solution, from the caproate (C_6) upwards, contains colloid. In the caproate only 15% is present in this form, while in the potassium stearate 99% is colloid. This is in accordance with former work from this laboratory, on appearance, washing power, density and conductivity.² The great increase in amount of colloid is in passing from the caprate (C_{10}) to the laurate (C_{12}) which about doubles it.

Again, in every case the amount of colloid falls off steadily and very readily with decrease in concentration. It appears to become inappreciable as measured at 0.2 *N* laurate; but since an error of 0.01° in the dew point is equal to 10% in the concentration in this dilute solution, it follows from previous work that some colloid is still present.

VII. *Only within certain limits can we at present allot the total colloid between micelle and neutral colloid.*—What we have so far established is the approximate total amounts of colloid and crystalloid present and the existence of ionic micelles which conduct as well as ordinary ions; and since the micelles conduct much better in concentrated solution, the total amount of colloid in such solutions as given in Tables X and XI, is somewhat too great.

The next step is to attempt to allot the total colloids and crystalloids among the 5 constituents which are present in concentrations of at least 0.01 *N*, namely sodium or potassium ion (given in Tables VI and VII), micelle, simple fatty ion, undissociated neutral colloid, and undissociated crystalloid. The results are given in Tables XII to XV according to each of 3 different assumptions. The upper figure in each case assumes that micelle tends to be formed much more than undissociated colloid, and so ascribes the total colloid to micelle as far as possible; the third makes the opposite assumption and favors undissociated colloid at the expense of micelle; the second allots the available colloid to both in the proportion of one fatty ion to one and a half molecules of undissociated soap. This middle value is certainly not far from correct in the concen-

¹ Bancroft thinks this possible (*Trans. Amer. Electrochem. Soc.*, 27, 124 (1915)). It is, however, not worth while considering the question at any length for we expect to be able to decide it by experiment (see *Trans. Chem. Soc.*, 105, 976 (1914), footnote).

² *Trans. Chem. Soc.*, 105, 435 (1914).

TABLE XII
Limits^a of Concentration of Colloidal Constituents of Potassium Salts

Weight normality	Stearate C ₁₈	Palmitate C ₁₆	Myristate C ₁₄	Laurate C ₁₂	Caprate C ₁₀	Caprylate C ₈	Caproate C ₆
Micelle ^b							
0.2	0.06	0.03	0.02	0.00	0.00	0.00	0.00
	0.02	0.01	0.01	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	0.21	0.20	0.24	0.22	0.14	0.07	0.02
	0.14	0.12	0.10	0.08	0.06	0.07	0.01
	0.06	0.01	0.01	0.00	0.00	0.00	0.00
0.75	0.31	0.35	0.37	0.38	0.28	0.17	0.08
	0.28	0.26	0.22	0.20	0.12	0.07	0.03
	0.23	0.24	0.16	0.14	0.00	0.00	0.00
1.0	0.41	0.45	0.49	0.52	0.44	0.28	0.15
	0.40	0.38	0.36	0.34	0.18	0.11	0.06
	0.40	0.40	0.40	0.37	0.00	0.00	0.00
1.5				0.70			
				0.62			
				0.75			
2.0				0.99			
				0.76			
				0.78			
Neutral Colloid ^c							
0.2	0.00	0.00	0.00	0.00	0.00	0.00	
	0.04	0.02	0.01	0.00	0.00	0.00	0.00
	0.06	0.03	0.02	0.01	0.00	0.00	0.01
0.5	0.14	0.11	0.03	0.00	0.00	0.00	0.00
	0.21	0.19	0.17	+0.14	0.08	+0.04	+0.01
	0.29	0.30	0.26	0.22	0.14	0.07	0.02
0.75	0.38	0.29	0.19	0.3	0.00	0.00	0.00
	0.41	0.38	0.34	0.31	0.16	0.10	0.05
	0.46	0.40	0.38	0.37	0.28	0.17	0.08
1.0	0.58	0.50	0.42	0.33	0.00	0.00	0.00
	0.59	0.57	0.55	0.51	0.26	0.17	0.09
	0.59	0.55	0.51	0.48	0.44	0.28	0.15
1.5				0.85			
				0.93			
				0.80			
2.0				1.00			
				1.13			
				1.11			

^a The upper number of each trio is calculated by ascribing the largest available proportion of the total colloid to micelle, the lowest similarly to undissociated colloid; the middle one which gives the most probable general idea assumes that 1.5 mols of undissociated soap are agglomerated for every mol of fatty acid that is so

^b Calculated as weight normality of agglomerated palmitate ion

^c This represents all the colloid other than agglomerated fatty acid ion. Whether a part of the whole is involved in the ionic micelle, or has a separate existence is a question which cannot be settled by the data represented here.

trated solutions, and altogether gives the fairest general picture of the composition of all solutions.

It will be noted that in some cases, especially where either colloid or crystalloid largely predominates, the concentrations are fixed within narrow limits; in some other cases these limits although definite are quite wide apart.

TABLE XIII.

Limits of Concentration of Crystalloidal Constituents of Potassium Salts at 90°.

Weight normality	Stearate C ₁₈	Palmitate, C ₁₆	Myristate, C ₁₄	Laurate, C ₁₂	Caprate, C ₁₀	Caprylate, C ₈	Caproate, C ₆	Acetate, C ₂
Simple Fatty Acid Ion								
0.2	0.01	0.05	0.07	0.11	0.14	0.15	0.15	0.19
	0.05	0.07	0.08	0.10	0.14	0.14	0.14	0.00
	0.07	0.08	0.09	0.10	0.14	0.14	0.14	0.15
0.5	0.00	0.00	0.00	0.04	0.14	0.23	0.29	0.45
	0.07	0.08	0.14	0.18	0.22	0.27	0.30	0.00
	0.15	0.19	0.23	0.26	0.28	0.30	0.31	0.32
0.75	0.00	0.00	0.00	0.00	0.12	0.22	0.35	0.00
	0.05	0.09	0.15	0.18	0.28	0.32	0.40	0.00
	0.08	0.11	0.16	0.24	0.40	0.39	0.43	0.45
1.0	0.00	0.00	0.00	0.00	0.08	0.25	0.37	0.78
	0.01	0.07	0.13	0.18	0.34	0.42	0.46	0.00
	0.01	0.05	0.09	0.15	0.52	0.53	0.52	0.58
1.5				0.00				0.00
				0.08				0.00
				0.05				0.80
2.0				0.00				0.00
				0.13				0.00
				0.11				1.01
Simple Neutral Undissociated Salt								
0.2	0.13	0.12	0.11	0.10	0.06	0.07	0.06	0.01
	0.09	0.10	0.10	0.11	0.06	0.08	0.07	0.00
	0.07	0.09	0.09	0.11	0.06	0.08	0.07	0.05
0.5	0.15	0.19	0.23	0.24	0.22	0.20	0.19	0.05
	0.08	0.11	0.09	0.10	0.14	0.16	0.18	0.00
	0.00	0.00	0.00	0.02	0.08	0.13	0.17	0.18
0.75	0.08	0.11	0.19	0.24	0.38	0.36	0.32	0.00
	0.05	0.02	0.04	0.06	0.19	0.26	0.27	0.00
	0.00	0.00	0.00	0.00	0.07	0.19	0.24	0.30
1.0	0.01	0.05	0.09	0.15	0.48	0.47	0.48	0.22
	0.00	0.02	0.04	0.03	0.22	0.30	0.39	0.00
	0.00	0.00	0.00	0.00	0.04	0.19	0.33	0.48
1.5	0.05	0.00
	0.13	0.00
	0.00	0.75
2.0	0.11	0.00
	0.62	0.00
	0.00				

TABLE XIV
 Limits of Concentration of Colloidal Constituents of Sodium Salts at 90°.

Weight normality	Stearate, C ₁₈	Palmitate, C ₁₆	Myristate, C ₁₄	Laurate, C ₁₂	Acetate, C ₂
	Micelle				
0.2	0.02	0.01	0.00	—0.03	0.00
	0.01	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00
0.5	0.17	0.20	0.22	+0.16	—0.03
	0.12	0.11	0.09	0.06	—0.05
	0.00	0.00	0.00	0.00	0.00
0.75	0.27	0.29	0.32	0.35	0.00
	0.23	0.22	0.19	0.17	0.00
	0.09	0.08	0.06	0.04	0.00
1.0	0.39	0.37	0.41	0.46	—0.23
	0.36	0.34	0.32	0.30	—0.09
	0.30	0.22	0.21	0.21	0.00
1.5	0.53	0.55	0.54	0.62	0.00
	0.68	0.64	0.79	0.58	0.00
	0.73	0.66	0.52	0.55	0.00
	Neutral Colloid				
0.2	0.00	0.00	0.00	0.00	0.00
	0.01	0.01	0.00	—0.03	0.00
	0.02	0.01	0.00	—0.03	0.00
0.5	0.13	0.05	0.00	0.00	0.00
	0.18	0.17	0.13	+0.10	—0.08
	0.30	0.28	0.22	0.16	+0.13
0.75	0.30	0.25	0.17	0.09	0.00
	0.34	0.32	0.30	0.27	0.00
	0.48	0.46	0.43	0.40	0.00
1.0	0.52	0.48	0.39	0.29	0.00
	0.65	0.51	0.48	0.45	—0.14
	0.61	0.63	0.59	0.54	—0.23
1.5	1.17	1.06	0.94	0.81	0.00
	1.02	0.97	0.69	0.86	0.00
	0.97	0.95	0.96	0.84	0.00

Whatever assumption is made, the absolute concentration of simple fatty ion is seen to rise at first with concentration, pass through a maximum and then nearly disappear, except that in extremely high concentration it may possibly increase again. The simple crystalloidal undissociated salt is similar but disappears rather more definitely.

Some ionic micelle and perhaps some of the other colloid are present in moderate dilution, but the amounts rapidly and steadily rise with concentration tending towards about $\frac{2}{3}$ of the total soap in the form of micelle and the other $\frac{1}{3}$ in the form of undissociated colloid. This is, by the way, a frequent approximate proportion for all the salts.

fatty acid radical, as is shown by the analyses of precipitates and sediments from soap solutions.

TABLE XV.

Limits of Concentration of Crystalloidal Constituents of Sodium Salts at 90°					
Weight normality	Stearate, Ca.	Palmitate Ca.	Myristate Ca.	Laurate, Ca.	Acetate, Ca.
Simple Fatty Acid Ion					
0.2	0.03	0.07	0.07	0.13	0.00
	0.04	0.08	0.09	0.17	0.00
	0.05	0.08	0.09	0.10	0.00
0.5	0.00	0.00	0.00	0.08	0.43
	0.03	0.09	0.13	0.14	0.35
	0.17	0.20	0.22	0.24	0.30
0.75	0.00	0.00	0.00	0.00	0.00
	0.04	0.07	0.13	0.18	0.00
	0.18	0.21	0.26	0.31	0.00
1.0	0.00	0.00	0.00	0.00	0.74
	0.03	0.03	0.09	0.16	0.60
	0.09	0.15	0.20	0.25	0.51
1.5	0.00	0.00	0.00	0.00	0.00
	-0.15	-0.09	-0.15	0.05	0.00
	-0.20	-0.11	+0.02	0.07	0.00
Simple Neutral Undissociated Salt.					
0.2	0.15	0.12	0.11	0.10	0.06
	0.14	0.11	0.11	0.11	0.06
	0.13	0.11	0.11	0.13	0.06
0.5	0.20	0.22	0.28	0.26	0.20
	0.15	0.13	0.15	0.16	0.28
	0.03	0.02	0.06	0.10	0.33
0.75	0.18	0.21	0.26	0.31	0.34
	0.14	0.14	0.13	0.13	0.34
	0.00	0.00	0.00	0.00	0.34
1.0	0.09	0.15	0.20	0.25	0.49
	-0.04	0.12	0.11	0.09	0.63
	0.00	0.00	0.00	0.00	0.72
1.5	-0.20	-0.11	0.02	0.17	0.84
	-0.05	-0.02	0.27	0.12	0.84
	0.00	0.00	0.00	0.10	0.84

The question now arises as to whether the undissociated colloid unites with the agglomerated fatty ions or whether, on the contrary, there are two independent colloids present, one highly charged and mobile, the other an ordinary colloid. The first view is certainly the more likely approximation to the facts but the question cannot be decided by the experimental data so far presented.

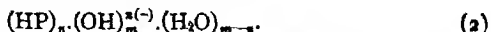
VII. *Some conceptions of the ionic micelle. Various hypotheses as to the genesis of the micelle lead to nearly the same result.*—Various views may well be taken with regard to the formation of the micelle.

stance, the simplest is to consider it as an agglomeration of palmitate ions, heavily weighted by water, a complex solvate:



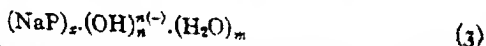
The water sphere, collected round these enormous electrical charges, is as inevitable as the collection of a droplet of water round an electron in saturated water vapor. Probably some at least of the undissociated colloid would also join in (see below).

This selfsame micelle can also be formulated thus



Here the assumption is complete hydrolysis of the palmitate ion followed by complete adsorption of the hydroxyl ions by the fatty acid. It is a question of taste as to whether such juggling attracts or repels the investigator. We personally appreciate it more when it appears to represent a difference in experimental result, not merely in words or even in standpoint.

Bancroft,¹ in discussing the preliminary accounts of our data, which had appeared before the outbreak of war suddenly stopped our scientific work, says: "As I see the matter, the sodium palmitate is hydrolyzed and the hydroxyl ions are adsorbed to a great extent by the undissociated palmitate and possibly by the insoluble palmitate acid also, though this seems less probable." The latter assumption is represented by Formula 2; the former by



leaving either n equivalents of insoluble palmitic acid or n equivalents of (insoluble) acid salt, say n NaHP, free in the solution. The former alternative of this pair for the solution is untenable since previous papers from this laboratory have shown conclusively that palmitic acid cannot exist in the free state in the presence of even the low concentrations of free hydroxyl ion characteristic of all these solutions. The latter alternative would mean that our undissociated colloid as tabulated in Tables XII and XIV consists of insoluble acid salt such as NaHP, or something intermediate between this and neutral NaP. One asks at once why NaHP, cannot adsorb hydroxyl ions too when it is exactly intermediate between the two substances HP and NaP which are proposed for this purpose in Formulas 2 and 3.

Much more important, however, is that Bancroft has evidently overlooked the existence of hydrogen soaps such as Reychler's cetyl sulfonic acid, of which hydrolysis is either out of the question or else becomes as arbitrary an assumption as that of a 100% hydrolysis of potassium chloride with ions such as KOH, $H^- + HCl.OH^+$ instead of $K^-.H_2O + Cl^+.H_2O$. Reverting to the idea expressed in Formula 1, that the micelle is built

¹ *Trans. Amer. Chem. Soc.* 40, 100 (1918).

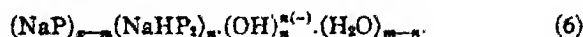
up around palmitate ions (or, if preferred, around other things adsorbing palmitate ions) the following formula seems the most plausible, where all or nearly all the colloid collects to form the micelle:



which is the same as follows:



or



The middle values given in Tables XII to XIV represent the micelle for the particular case:



The only argument that occurs to us for regarding adsorbed hydroxyl ion as the basis of the micelle is that it is in general comparatively readily adsorbed. However, a more than 99% adsorption in a highly concentrated solution would differ wholly and remarkably from hitherto investigated cases of sorption.

The formulas above present only a general scheme for the micelle. Their composition must alter continuously with the concentration or upon the addition of salts. Thus in very concentrated solution or in the presence of large amounts of another electrolyte such as sodium hydroxide (see below), the soap must be nearly all colloid of approximately the composition



In other words, the question left open is as to whether in moderate concentrations the micelle has Formula 4, corresponding to (8) less the sodium which has gone to form ions and plus the equivalent number of electrical charges on the palmitate radicals left, or, on the other hand, has a formula such as (1) (where the value of x in Formula 4 has become very small). If the first is the case, the micelle alters gradually from (4) to (8) as the dissociation is driven back; on the second alternative, driving back the dissociation does not alter the composition of the ionic micelle so much, but replaces it by producing neutral colloid instead. Here it must be remembered that in dilute solution simple, neutral, crystalloidal, undissociated soap does exist independently.

With regard to the value of n , the number of negative charges on one micelle, it must be at least 10, and may be much greater. There the "molecular weight" of one ionic micelle must be nearly 3000 anyway since the true molecular weight of the palmitate ion is 255. Similarly the enormous molecular weights ascribed to various substances which occur only in colloidal form may be derived from the aggregation of comparatively small molecules.

VIII. *The effect of concentration upon the ionic micelle excluding the*

ions had not been studied. The results are presented in Table XVI. It was not considered necessary to correct the dew points for the effect of the partial pressure of the ammonia as it was evidently too small.

TABLE XVI.

TABLE XVI—DEW-POINT MEASUREMENTS ON AMMONIUM SOAPS

Soap	Weight normality	Temperature °C	Rise in boiling point °C	Concentration of total crystalloid <i>N</i>	Van't Hoff's factor <i>i</i>
NH ₄ Laurate C ₁₂	1 0	25	0 37	1 22	1 22
NH ₄ Laurate C ₁₂	0 5	25	0 16	0 53	1 06
NH ₄ Laurate C ₁₂	0 25	25	0 00	0 30	1 20
NH ₄ Laurate C ₁₂	1 0	45	0 42	1 19	1 19
NH ₄ Palmitate C ₁₆	1 0	25	0 08	0 26	0 26
NH ₄ Palmitate C ₁₆	1 0	45	0 07	0 20	0 20
NH ₄ Palmitate C ₁₆	1 0	90	0 13	0 27	0 27

In warm weather the *N* and 0 5 *N* laurates were quite clear solutions, showing none of the usual appearances of soap solutions except that they gave a very good lather. On cooling under the tap the 0 5 *N* laurate solution deposited feathery crystal-like flakes; the *N* solution would not do this, but in very cold weather is set to a semi-transparent jelly similar to a potassium soap. The 0 2 *N* palmitate was somewhat similar but the *N* solution was practically solid at all temperatures and resembled fine, white, solid foam.

A glance at the results shows that, independent of the temperature, there is a very big difference between the two kinds of soap, very much greater than that observed in the potassium soap solutions. The total crystalloids are about twice as great for the laurates and half as great for the palmitates as compared with the case of the potassium or sodium soaps. An appreciable fraction of the total crystalloid will be undissociated ammonia.

Further investigation would evidently be well repaid, particularly if pure fatty acids be used for making the solutions and hydrolysis be avoided as suggested above. Enough has been presented to show that the relationships here agree with our general conception of colloidal electrolytes.

X. *In mixtures of soaps the tendency is to form more micelle. Additions of electrolytes exert opposing influences, dehydrating and driving back dissociation.*—All commercial soaps are mixtures, hence the importance of the study of mixtures, which must, however, be preceded by a knowledge of pure constituents. Our data for the conductivity of mixtures of sodium soaps are very scanty, but they show that the conductivity differs but slightly from that calculated from the components separately. Thus a 0.1 *N* soap solution which is 0 05 *N* each with regard to palmitate and to myristate or laurate conducts at least 98% as well as the mean of 2

pure 0.1 *N* solutions alone.¹ These concentrations are of course too low for the effect of the micelle to be observed.

The usual tendency is for the conductivity of the mixture to be just slightly higher than expected, as appears from measurements recently published by Kurzmann,² working with F. Goldschmidt. In mixtures of 0.6 *N* potassium oleate with 0.2 *N* potassium laurate, he found an increase in conductivity above that of the constituents separately of 5% and 3.6% at 20° and 90°, respectively. Using 0.4 *N* oleate and 0.6 *N* laurate, the effect is an increase of about 4% in the conductivity at 20° but a lowering of about the same amount at 90°.

TABLE XVII MISCELLANEOUS DEW-POINT RESULTS.

Substances	Weight normality	Temperature °C	Rise in boiling point °C	Concentration of total crystalloid %	van t Hoff's <i>i</i>
NaCl*	0.25	90	0.23	0.45	1.92
NaCl*	0.5	90	0.45	0.93	1.86
NaCl*	1.0	90	0.85	1.76	1.76
KCl*	1.0	90	0.86	1.78	1.78
K Caprylate (C ₈)	3.0	20	1.01	3.47	1.16
Na Palmitate (C ₁₆)	0.25	90	0.14	0.29	1.16
Na Palmitate (C ₁₆)	1.0	90	0.25	0.52	0.52
Na Palmitate (C ₁₆)	1.0	70	0.23	0.56	0.56
K Laurate (C ₁₂)	0.2	20	0.11	0.38	1.90
K Laurate (C ₁₂)	0.2	90	0.15	0.31	1.55
K Oleate (C ₁₈ -H ₃)	0.6	20	0.21	0.72	1.20
K Oleate (C ₁₈ -H ₃)	0	90	0.25	0.52	0.86
{ Na Palmitate (C ₁₆)	0.25	90	0.21	0.43	0.86
{ K Palmitate (C ₁₆)	0.25				
{ Na Palmitate (C ₁₆)	0.25	90	0.34	0.70	1.55
{ NaCl	0.20				
{ Na Palmitate (C ₁₆)	1.0	90	0.49	1.01	0.81
{ NaCl	0.25				
{ Na Palmitate (C ₁₆)	1.0	90	0.87	1.80	0.93
{ NaOH	0.927				
{ K Laurate (C ₁₂)	0.2	20	0.33	1.13	1.51
{ K Oleate (C ₁₈ -H ₃)	0.6				
{ K Laurate (C ₁₂)	0.2	90	0.36	0.74	0.95
{ K Oleate (C ₁₈ -H ₃)	0.6				

* The sodium and potassium chlorides agree within the experimental error with the acetates.

¹ E. C. V. Cornish, 1913, unpublished work.

² J. Kurzmann, Dissert. 1914, also *Kolloid Chem. Beihefte*, 5, 427 (1914). He finds the conductivity of 0.6 *N* potassium oleate to be nearly that we have found for potassium palmitate, but judging from the difference between his and our conductivity data the conductivity might possibly be nearer that of potassium myristate (C₁₄). Our dew-point lowering is like that of potassium myristate. Thus the effect of the one unsaturated bond is to lower the oleate which corresponds to stearate (C₁₈) in the homologous series. This agrees with its other properties.

Table XVII contains a few measurements of the dew-point lowering of mixtures, including the first pair just cited. This mixture exhibits at 90° a dew-point lowering of 0.36° as compared with 0.40° , the sum of the constituents taken separately. At 20° this is reversed, for the mixture gives 0.33° instead of 0.3° calculated.

It is evident that several factors would be involved. First would come the driving back of dissociation owing to the increase in total concentration of the common ion. Second, another influence tending to form micelle is the opportunity for formation of mixed ionic micelle, comprising both constituents. Third comes the dehydrating effect which all crystalloid mixtures must exert (see below); this will be greatest when the soap is most crystalloidal, and will tend to diminish formation of micelle.

The solution in Table XVIII containing $0.25\text{ }N$ sodium palmitate together with $0.25\text{ }N$ potassium palmitate gives a lowering of 0.21° , as compared with 0.20° and 0.19° for $0.5\text{ }N$ solutions of the pure constituents respectively, or with 0.27° , which is the sum of the results for $0.25\text{ }N$ solutions taken separately.

The small experimental effect upon conductivity and osmotic activity when soaps are mixed does not preclude fairly extensive alterations in the equilibria involved and to be expected from our explanation. This is illustrated by Kurzmann's¹ observations on the viscosity of the mixture of oleate and laurate we have discussed above. Both at 20° and 90° the viscosity is intermediate between solutions of the two constituents if taken separately but in the same total concentration. If merely taken separately the viscosity of the mixture at 90° is not quite the sum of that of the constituents. At 20° , however, the $0.6\text{ }N$ oleate alone has a viscosity equal to 1573, the $0.2\text{ }N$ laurate alone 141, the mixture 329, which is over 6 times the viscosity of $0.8\text{ }N$ laurate 497.

In the case of mixtures with electrolytes, the influences are at least two-fold and in the opposite direction. First comes the dehydrating effect which every lowering of vapor pressure must exert and to which these heavy hydrated micelles must be extraordinarily sensitive. This will tend to diminish their formation and also to make the solution less viscous. Opposed to this is the second effect which tends to drive back dissociation and which ultimately salts out the greater part or all of the soap. In appreciably concentrated solutions, as already fully explained, the observed osmotic results will tend to appear greater than they really are, owing to the hydration.

The first effect discussed is already familiar through the work of F. Goldschmidt and co-workers¹ and also of Farrow² on viscosity. This viscosity of $0.25\text{ }N$ sodium palmitate is lowered at 70° by about 10%

¹ *Loc cit*

² *Trans. Chem. Soc.* 101, 747 (1912)

when it contains 0.07 *N* sodium chloride; further addition rapidly increases the viscosity above this minimum to values many times greater than that of the original soap solutions. The explanation given at the time by Farrow recognized this as a general property of colloids (the illustrations cited were really colloidal electrolytes) and likewise attributed it to dehydration, but he discussed it from the now rather discredited standpoint of the emulsion theory of colloids. The second effect is also clear from the ultimate salting out.

Both effects will be most pronounced when there is most micelle and when the micelle is most hydrated. On turning up Kurzmann's data we found as expected, that the dip in viscosity was greater for oleate and less for laurate, that the subsequent large rise in viscosity occurred sooner when adding electrolyte to oleate than to laurate, that both minimum and subsequent rise requires more addition at higher than at lower temperatures where we consider hydration to be greatest. In the case of the ammonium soap from palm kernel oil the second effect appears to over-ride everything else when ammonium chloride is added. In the cases in Table XVII, the dew point lowering of the mixtures with 0.20 and 0.25 *N* sodium chloride exceeds the sum of the constituents by an amount 0.01°, within the experimental error. On the other hand, with stronger solution, namely 0.1 *N* sodium palmitate and 0.93 sodium hydroxide, the observed lowering of 0.87° exceeds that of the alkali alone by only 0.05° instead of the 0.25° which the palmitate alone would produce. Here it is evident that the palmitate is already largely pushed back into undissociated soap or that the micelle is tending towards Formula 8, that is, undissociated neutral soap as discussed above. Data on this question will be contained in another communication from this laboratory.

XI. *At lower temperatures there is more micelle and it is more hydrated.*—As can be observed even from the data of Table XVII, in every case the apparent osmotic effect is relatively somewhat greater at lower temperatures, but this will be dealt with in a separate experimental communication.

However, it is worth pointing out that the very high temperature coefficient of conductivity which we have established in earlier papers and which has also been formed by F. Goldschmidt and others, is apparently due to hydration increasing as the temperature falls. This is strongly supported by the enormous increase in viscosity with lowering of temperature which has been measured by F. Goldschmidt and his collaborators.

On heating a soap solution to a constant high temperature, the lowering of dew point is at first slightly too great, but it rapidly falls to a constant value. On cooling the opposite is observed. Similarly, in an earlier paper from this laboratory, the conductivity of a sodium soap suddenly raised to a higher temperature is at first slightly too great and *vice versa*

XII. *Some data for extreme concentration.*—Table XVIII presents the dew-point lowering and the vapor pressures of sodium palmitate solutions measured to quite extreme concentrations. Up to 0.5 *N* solutions the data are found in Table III. There each solution was made up independently, maximum lowering being observed in 1.0 *N* solution, a minimum in 1.5 *N* solution. Owing to the great difficulty in preparing and handling these "solutions," the higher concentrations were attained by pumping out the water vapor through weighed tubes containing calcium chloride. The amount of water remaining in the soap solution, and hence the concentration, was determined sometimes by direct weighing, sometimes by weighing the calcium chloride tubes, sometimes by both methods. The table combines 4 series of measurements. In every case time was allowed for the vapor pressure to become constant (usually one hour was found sufficient for this). Addition of small amounts of water proved that the operation was quite reversible. Using a good water pump and keeping the soap at 90° for many hours, the proportion of water never was reduced below $H_2O : NaP = 1 : 1$. In 2.3 weight-normal solution (24 mols of H_2O to one of NaP) small star-shaped clusters of crystals appeared on the side of the tube, the bulk of the soap was silky, resembling 0.2 *N* sodium laurate, and would not foam easily. On further evaporation these crystals disappeared, the soap became more liquid and foamed more readily, but ultimately became more solid again. The fourth and fifth columns of Table XVIII have probably no real meaning but assist in appreciating the order of magnitude of the results and in showing that the lowering finally becomes proportional to the weight normality.

TABLE XVIII
Dew-Point Lowering of Extreme Concentrations of Sodium Palmitate at 90°

Weight normality	Mols H_2O to 1 NaP	Lowering °C	Concentration of crystalloid	van t Hoff's i factor	Actual vapor tension Mm
1.5	36.65	0.22	0.455	0.30	521.9
1.62	34.27	0.27	0.56	0.35	520.6
1.74	31.89	0.33	0.68	0.39	519.4
1.9	29.21	0.40	0.83	0.44	518.1
2.0	27.75	0.50	1.04	0.52	516.1
2.41	23.02	0.86	1.78	0.74	509.1
3.0	18.49	1.23	2.55	0.85	501.9
4.22	13.15	1.32	2.73	0.65	500.3
8.12	6.83	2.64	5.48	0.67	475.4
12.56	4.42	4.26	8.82	0.70	446.5
14.29	3.88	4.72	9.77	0.68	438.6

XIII. *The action of typical dyestuffs and indicators such as congo red may be similarly explained.*—As we have for many years insisted, any final theory of soap solutions—

derstanding the properties of dyes, acid and alkali albumens and many other complicated cases.

According to the theory of colloidal electrolytes here presented, in every case we expect to find pronounced electrical conductivity co existing with deficient osmotic activity.

All recent work on the osmotic activity of dyes has been based upon the use of an osmometer. The results require much interpretation on account of various factors such as Donnan's "membrane equilibrium" which may completely obscure the purely osmotic effect in question. It is a distinctive advantage which our dew-point measurements on soaps possess, that all such complications are excluded. This is the reason why the present data constitute by far the most definite study yet made of the osmotic pressure of colloids.

The work of Donnan and Harris,¹ in agreement with that of Bayliss² and Biltz and Vegesack,³ shows that the osmotic pressure of congo red is considerable, but does not exceed that of a simple non-electrolyte. On the other hand, the conductivity was unexpectedly high, being nearly equal to that of sodium chloride. Donnan's interest was chiefly attracted to the important theory of membrane equilibria, which he thought might be sufficient explanation of the discrepancy, since the sodium ions were not expected to contribute in the ordinary way to the osmotic pressure. He discussed the formation of high complexes such as $(\text{Na}_2\text{R})_{20} \rightleftharpoons 20\text{Na} + (\text{NaR})_{20}'$, but added, "it is difficult to reconcile such an assumption with high values obtained for the molar conductivities." The explanation we advance is that described under Section II.

On the other hand Bayliss,⁴ whose paper, unfortunately, we have only recently read, writes, after making various alternative suggestions, "The possibility of aggregated simple ions carrying the sum of the charges of their components is suggested in order to explain the experimental results." Further, "These large organic ions may aggregate while retaining the combined charges of their components. This seems to imply however, so great a density of the charge on the surface of the aggregates as to be improbable. * * * * * The difficulty as to the large charge on the aggregated anion remains * * * * * It may be tentatively suggested that aggregation of molecules may play some part in the mode of ionization."

Again, the mechanism⁵ suggested by one of us removes the theoretical difficulty, and this hypothesis reconciles the osmotic effects, the colloidal effects, and the conductivity data.

¹ *Trans. Chem. Soc.*, 99, 1554 (1911)

² *Proc. Roy. Soc., B*, 84, 229 (1911) and earlier papers.

³ *Z. physik. Chem.*, 73, 481 (1910); 77, 91 (1911), etc

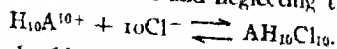
⁴ *Loc. cit.*

⁵ *See also Donnan and Harris, loc. cit.*

The existing data for other dyes and for indicators are of a similar nature and may be similarly accounted for. Many of the unexplained reactions of indicators, particularly with reference to the sometimes enormous effect of neutral salts, are now seen to be probably due to disturbance of the equilibria between colloid and crystalloid and hence between the various possible crystalloidal forms of the indicator radical. We have proven that such true equilibria occur, and that every change in the colloid, conditions a corresponding alteration in the position of equilibrium.

XIV. *The explanation here advanced accords with the data for proteins. Very slight alteration in concentration may condition large displacements of the equilibria*—In 1913, in a general discussion held by the Faraday Society, W. Pauli summarized the data hitherto obtained relating to investigations of the viscosity and electrochemical properties of protein solutions¹ and deduced a heavily hydrated polyvalent ion. McBain pointed out how the outstanding conflicting data were reconciled by the explanation advanced in Section II. Reference must be made to the papers cited for the details of Pauli's masterly summary, to see how far these investigations have already been carried. A point of great interest for the case of soap solutions may, however, be mentioned; that is, the effect of concentration upon equilibria involving micelles. Manabe and Matula, working with Pauli, have re-examined electrometrically the combination of albumen with each ion of hydrochloric acid.² The maximum difference between the amounts of hydrogen and chlorine ions taken up by 1% albumen occurs at about 0.02 *N* hydrochloric acid showing maximum formation of ionized salt. This maximum coincides with maximum viscosity and maximum osmotic effect in an osmometer. Further addition of hydrochloric acid drives back the ionization with extreme rapidity.

This very great influence of concentration is only what is to be expected from the principle of mass action. The law of mass action will probably never apply in quantitative form, but it will possess semi-quantitative or at least qualitative value. Thus, in the equilibrium between albumen and its ions where *A* represents the albumen radical, supposing for example the micelle to be decavalent and neglecting the hydration,



Here the ionization should depend upon the tenth power of the chlorine ion, so that doubling the concentration of hydrochloric acid may quite well have the very great effect found by Pauli. Were the case of the soap micelle exactly similar, doubling the concentration of say a 0.5 *N* sodium palmitate solution should have an extremely great effect on the dissociation.

¹ *Trans. Faraday Soc.*, 9, 54 (1913); and *Kolloid Z.* 1913, 1914, 1915.

tion of the electrolytic colloid. This, however, is not observed (see Tables VII, XIV and XV). We must conclude that there is some partly compensating factor, and the obvious suggestion is a difference in amount of hydration of the palmitate micelle as the concentration increases. This had already been deduced in Section V on quite different grounds.

We should like to point out that in the case of most ions and of ionic micelles in general where there may be a series of solvates containing up to many molecules of solvent in one particle, a similar consideration must apply. That is, even the very small relative lowerings of vapor pressure of solvent observed in ordinary solutions must exert a large influence on the composition as well as upon the amounts of each solvate present. For example, if the solvation of lithium ion is, say, 10 molecules of water in 0.1 *N* salt solution, for which the vapor pressure lowering is about 0.3%, doubling the concentration of the salt nearly doubles the vapor-pressure lowering, making it, say, 0.6%. This altered vapor pressure has to be raised to about the tenth power according to the mass law in order to compute its influence on the solvation of the decahydrate. The tenth power of 99.4% is 94.2%; therefore, the equilibrium will be shifted so that about 6% of the decahydrate disappears owing to this cause. This result is not affected by any other possible co-existing equilibria with, say, nono- or octahydrate, and it is a very large effect. We hope to return at another opportunity to the bearing upon the dissociation theory of this suggestion for a solvate theory.

Pauli, in correspondence with one of us in 1914, expressed his concurrence in the general explanation of colloids which we have described in the present communication. Apparently he has applied it to the case of sols of ferric hydroxide,¹ finding them to consist of a moderately dissociated electrolytic colloid with chlorine ion as anion and an ionic micelle as cation. If our explanation is correct, there will almost certainly be a gradual transition from typical ionic micelles to ordinary ions, on the one hand, and to electrically neutral suspension colloids on the other.

Summary.

1. For the first time a comprehensive theory of soap solutions has been set up.
2. This has led to a definition of colloidal electrolytes, a class whose members will probably prove more numerous than acids and bases put together.
3. These colloidal electrolytes are salts in which one of the ions has been replaced by an ionic micelle.
4. It is evident that this is an extension of the dissociation theory, in that there is a gradual transition from ordinary electrolytes (true salts and complex ions to typical colloidal electrolytes.

¹ *Kolloid-Z.*, 31, 49-63 (1917); through *J. Chem. Soc. Abstr.*, 112, II, 563 (1917).

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5. This is exemplified by any one of the higher soaps simply on change of concentration. Thus in concentrated solution there is little else present than colloid plus cation, whereas in dilute solution both undissociated and dissociated soap are crystalloids of simple molecular weight.

6. Similarly, there is a continuous transition from typical colloidal electrolytes through slightly charged colloids to typical neutral colloids.

7. For the summary of the chief properties of the soap solutions, reference should be made to the numbered statements used as headings in the present paper. These follow from the mass of dew point data here presented, by which Krafft's well known but erroneous results for "molecular weights" of soaps are at last superseded.

8. The ionic micelle in the case of soaps exhibits an equivalent conductivity quite equal to that of potassium ion. Its formula may correspond to $P_n^{+(-)}mH_2O$ but more probably it is $(NaP)_n P_n^{+(-)}(H_2O)_m$, where P^- is the anion of the fatty acid in question.

In conclusion, we desire to express our thanks to the Colston Society of the University of Bristol for substantial grants towards the purchase of materials and apparatus. Finally, our thanks are due to Miss M. E. Laing for her assistance in preparing this paper for publication, without which its appearance would still have been indefinitely delayed.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE COAGULATION OF CLAY SUSPENSIONS AND SILICIC ACID.¹

BY OTTO M. SMITH

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An explanation is given in this paper of why many turbid river waters require at certain periods excessive amounts of coagulants for clarification and how purification may be most efficiently accomplished. The action of electrolytes commonly occurring in natural waters upon the stability of colloidal clay suspensions and silicic acid and their effect when alum is used as a coagulant, is discussed. Colloidal clay and silicic acid are more prevalent in the surface waters of the Mississippi valley² and the western states, and the need of research in this line has been emphasized in several papers.³

The experimental work was carried out along 3 well defined lines, and is discussed in the following order: 1. The removal of silicic acid

¹ Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

² Water Supply Paper No. 236

³ Fuller, "Water Purification at Louisville, Ky.," *Elms, Eng. Record*, 51, 552; Black and Veach, *ibid.*, 72, 292, and Catlett, *ibid.* 72, 721.

from dilute solutions by electrolytes and colloids 2. The effect of electrolytes on dilute clay suspensions. 3 The effect of silicic acid on the coagulation of clay suspensions in the presence of electrolytes.

Precipitation of Silicic Acid.

Silicic acid is not precipitated from a solution containing 184 parts per million of silica by solutions of sodium chloride, sodium carbonate, sodium hydrogen carbonate, sodium sulfate, potassium sulfate, trisodium phosphate, magnesium hydrogen carbonate, magnesium sulfate, barium chloride, calcium chloride, aluminum sulfate, ferrous sulfate, ammonium sulfate, ferric chloride and aluminum chloride, when present in a concentration of 0.07 *N*, but is precipitated by sodium, calcium and barium hydroxides and colloidal iron at a concentration of 0.099 *N*, 0.0019 *N*, 0.0019 *N* and 0.0045 *N*, respectively.

Temperature Ca. 23°		Time, 5 minutes.	
Ca.	<i>N</i> .		<i>N conc.</i>
5 5	0.18	NaOH	0.099
0 6	0.018	Ca(OH) ₂	0.0019
0 4	0.026	Ba(OH) ₂	0.0019
2 6	(0.6 mg.)	colloidal Fe	0.0045

These results indicate that bivalent ions have a precipitating value 50 times that of monovalent ions. Trivalent ions from the formula $1 : x : x^2$ should have a coagulating value of 2500 times that of the univalent and 50 times that of bivalent ions. Qualitative experiments with more dilute solutions indicate that the ratio between bivalent and trivalent to be about one to four. The more dilute a solution, the less marked is this precipitating effect of the cations.

Very dilute solutions—30 or 40 parts per million of silica—are not precipitated by sodium hydroxide and rather high concentrations of calcium hydroxide relative to silicic acid are necessary to obtain a precipitate within 6 hours. At these concentrations the reactions may be ionic and precipitates of calcium silicates may be thrown down. Since the hydroxides of calcium and barium precipitate silicic acid, it is desirable to know the effect of added univalent and bivalent ions upon the amount of calcium hydroxide needed.

To 5 cc. of a dialyzed silicic acid solution, containing 625 parts per million of silica, there was added 0.5 cc. of a 0.1 *N* solution of the above electrolytes and the silicic acid precipitated by the addition of calcium hydroxide. Precipitation resulted when 0.3 cc. of calcium hydroxide was added to solutions of barium, calcium, magnesium, iron and aluminum more than this being required in all other cases. The result was not influenced by sodium chloride at these concentrations. It is evident that the precipitating value of the cation depends upon its valence and that the hydroxyl has some influence.

Accordingly the concentration of the hydroxyl ion necessary before silicic acid is precipitated by calcium hydroxide from its solution in water alone or when any of the salts mentioned above are present, was determined and found to correspond to between a P_H ¹ of 8.6 and 9.5. Silicic acid may act as a buffer in the manner of large complex organic molecules because there appears to be little relationship between the normality or alkalinity of the solution and the concentration of the hydroxyl ion.

The optimum conditions, according to the theory of coagulation, for precipitation of negatively charged silicic acid, should be: (1) an amount of trivalent cations or positively charged colloids sufficient to neutralize exactly the negative charges; (2) a minimum amount of univalent cations, protective or stabilizing colloids and (3) the same P_H value as that at the iso-electric point. Just what conditions must be defined in order to locate the iso-electric point, have not been discovered. Flemming² designated it in terms of normality of the solution, but it seems preferable to express it by the concentration of the hydrogen ion.

Since the above tests indicate that the optimum P_H value for the precipitation of silicic acid is approximately 9.0, the maximum amount of silicic acid ought to be removed when the reaction is carried out at this point, and in order to determine this value more accurately and in the absence of bivalent cations, aluminum hydroxide was precipitated in the silicic acid solution by sodium hydroxide and aluminum chloride, and the relationship observed between the removal of silicic acid, the concentration of the hydroxyl ion and the character of the precipitate.

The acid was prepared by bringing the solution of sodium silicate to a P_H value of 6.5 by the addition of hydrochloric acid. This solution contained 4 mols of silicon dioxide to one mol. of sodium chloride. Two dilutions were used: 87 and 232 parts per million of silicon dioxide. To the silicic acid solution were added water to produce the proper dilution, aluminum chloride and 0.1 N sodium hydroxide solution, which was added drop by drop with constant shaking. After shaking at frequent intervals and standing 48 hours, the reaction was practically complete. The solution was filtered and silicic acid determined in the filtrate. It was noticed in precipitating aluminum from a solution of aluminum chloride, silicic acid and sodium chloride, that the manner of adding the reagents and the relative ratio of aluminum to silicic acid markedly influenced the character and amount of the precipitate.

Poor removal of silicic acid is associated with a turbid colloidal solution and a sticky gelatinous precipitate which is very difficult to filter while a good removal is usually obtained when the precipitate is well flocculated and settled quickly from a clear solution which exhibited little

¹ Determined by the colorimetric method of Clark and Lubs, $P_H = -\log C_H$.

² *Z. physik. Chem.*, 41, 443 (1902)

Tyndall effect. In the absence of silicic acid a flocculent precipitate of aluminum hydroxide was produced in a dilute solution of aluminum chloride by 0.1 *N* sodium hydroxide solution or in a dilute solution of sodium hydroxide by 0.0003 *N* aluminum chloride regardless of the manner of adding reagent or presence of sodium chloride. If the above solution contained 87 parts per million of silica as colloidal silicic acid, on adding 0.1 *N* sodium hydroxide drop by drop, a precipitate formed at the end of one hour, depending upon the amount of aluminum chloride in the solution, but if an equivalent amount of 0.1 *N* or stronger sodium chloride was added all at once no precipitate formed. The later solution showed a very strong Tyndall effect and gradually deposited a small amount of very fine precipitate. One solution was made from which very little precipitate settled at the end of a month. The same effect was produced when sodium hydrogen carbonate or carbonate was used instead of hydroxide.

With calcium hydroxide an excellent precipitate formed regardless of the manner of adding the reagent. There are evidently some complex substances formed under these conditions, which are intimately connected with the sodium ion and the silicic acid. Perhaps the silicic acid in the presence of sodium ions is acting as a protecting colloid preventing in some manner passage of aluminum hydroxide from the colloid into the crystalline condition. In any event, the importance of this fact is quite valuable in obtaining well flocked precipitates. A high ratio of silicic acid to aluminum tends to produce colloidal solutions while the reverse ratio produces nicely flocked precipitates. The magnitude of the Tyndall effect is inversely related to the removal of the silicic acid and the character of the flock or precipitate.

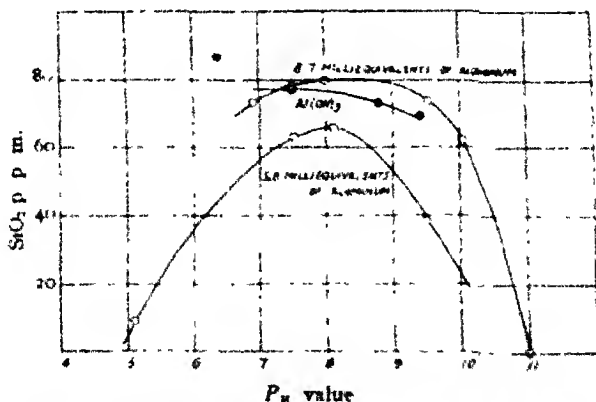


Fig. 1.—Comparison between the P_H value, the precipitation of silicic acid and the amount of $Al(OH)_3$ in the solid phase.

Thus in plotting the curves, Fig. 1, Table I, only the higher concentrations of aluminum salt are used; the lower values are inaccurate because of the formation of colloidal solutions. There is shown in Fig. 1 a third curve, obtained by precipitating the aluminum with ammonia in the absence of silicic acid.

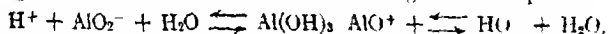
TABLE I.

Removal of Silicic Acid^a by Aluminum Hydroxide of Various Hydrogen Ion Concentrations

Millequivalents of Al	Temperature 62.23°. Time, 48 hours		P_H
	SiO ₂ precipitated	SiO ₂ in solution	
8.73	73	14	6.4
8.73	79	8	7.5
8.73	79	8	8.0
73	74	13	9.6
8.73	0	87	11.0 no ppt.
5.82	9	78	5.2 colloidal
5.82	93	24	7
5.82	65	22	8.2 colloidal
5.82	38	49	9.5

^a Concentration of SiO₂ is 87 parts per million

A study of data and curves indicates (1) that silicic acid is best precipitated at a P_H value of 8.0 to 8.5, (2) that the amount of silicic acid precipitated follows closely the amount of aluminum hydroxide in the solid phase, and (3) that below a P_H value of 4.0 the concentration of the hydrogen ion shifts the reaction so far to the right in the equation:



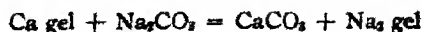
and that above a P_H value of 11.0 so far to the left that the solid aluminum hydroxide phase is unstable and disappears.

In the region below these curves the tendency to form colloidal solutions is quite marked and the gelatinous nature of the precipitate and the magnitude of the Tyndall effect generally varies inversely with the amount of aluminum ions added to the system and directly as the hydrogen ion concentration departs in either direction from a P_H value of 8.25.

The precipitation of silicic acid by aluminum sulfate may probably be explained by (1) the neutralization of the charge on the silicic acid complex by the aluminum ion, (2) by the neutralization of the negatively charged silicic acid by positively charged aluminum hydroxide, (3) by the solid aluminum hydroxide adsorbing the silicic acid or (4) by the formation of an insoluble chemical compound.

The Coagulating Action of Electrolytes on Clay Suspensions.

If sodium carbonate or an acid be added to a clay which has just enough calcium to keep the colloidal matter in the gel form, it may react according to the following equation:



or



Much valuable information is available in the ceramic researches on the action of salts on clay suspensions. The work of many investigators on clay slips (a suspension of clay in water whose consistency is that of thick cream) indicates that sodium, potassium and lithium hydroxides, carbonates, silicates and sulfides generally have a high dispersive or stabilizing power while the most active coagulating agencies are the salts of the bivalent and trivalent cations especially in the presence of a high concentration of hydroxyl ions

The above agrees with the statements of Mayer, Schaffer and Terroine¹ that the addition of a trace of alkali decreases the size of the negative suspended particles and Hardy's conclusions that the coagulation of a negative sol varies directly as the valence of the cation and that the action of the anion obeys the regular ionic laws

The above observations were obtained from rather concentrated clay suspensions where the ultimate end was the formation of a stable fluid slip of the highest clay content. In water purification, on the other hand, the aim is the removal of a very small amount of colloid material from a large amount of water. It is clearly evident from a study of dilute clay suspensions and colloidal silicic acid that the physical state of the substances and their chemical properties must be taken into consideration, and the factors which influence them, i. e., (1) degrees of dispersion, (2) the presence of the protective colloids and adsorbed substances, (3) magnitude and kind of electric charge, (4) the liquid or dispersing medium, (5) the ionic content of the liquid, (6) the concentration, (7) the temperature and (8) the speed of reaction of added substances.

Washed potters clays were used in making the suspensions. Tennessee ball clay Nos. 1 and 3 remained longest in suspension. Ashley rates the latter as having a relative colloid content of 95 to 100%. The clay was freed from large particles and soluble salts by washing with distilled water and running the suspension through a Sharples supercentrifuge; the desired end being a suspension as nearly like that in surface waters, but free as possible from electrolytes. These suspensions had turbidities of 400 to 420 and coefficients of fineness of 0.79 to 0.81. Standards for determining turbidities were prepared from original clay suspensions and checked with a standardized turbidimeter.

Fine particles of various sizes in suspension do not settle uniformly leaving a clear supernatant liquid, but are deposited in layers or zones. Those particles of approximately the same diameter will settle together leaving a turbid suspension of finer particles above. In a suspension one

¹ *Compt. rend.*, 145, 918 (1907).

can observe 2 or 3 of these zones of widely different turbidities and rates of sedimentation. Within a zone the turbidity is fairly uniform, but different zones vary as much as 100¹¹⁷/₀ within a vertical distance of 1/2 inch.

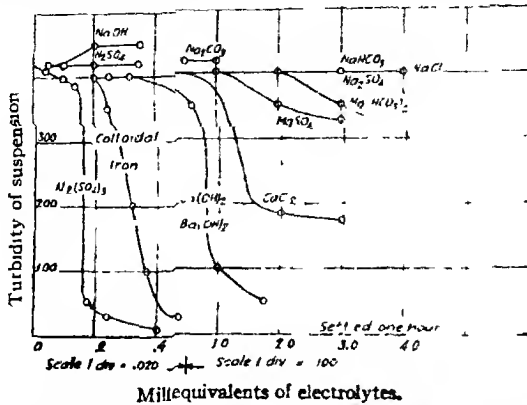


Fig. 2.—Effect of electrolytes on the coagulation and settling of clay suspensions.

It was necessary to determine the turbidity of a suspension without disturbing the liquid. A beam of parallel rays of light 3/16 inch in diameter from a stereopticon equipped with a 500-watt lamp was projected through the standard and sample, parallel to and 3/4 inch below the surface of the

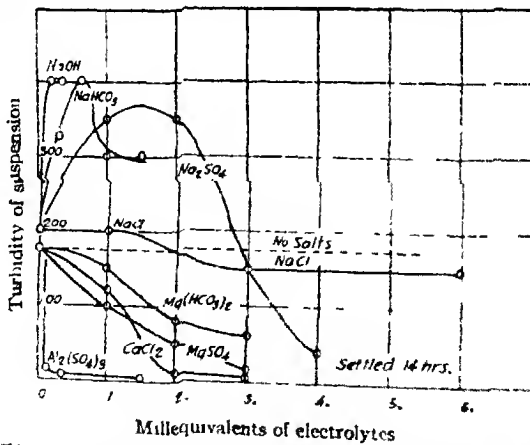


Fig. 3.—Effect of electrolytes on the coagulation and settling of clay suspension.

liquid in the bottles, and the turbidity determined by observing the intensity of this beam of light.

Reagents were added to 100 cc. portions of the clay suspension and thoroughly mixed by shaking for one minute; the samples were then al-

lowed to remain perfectly quiet at room temperature and the turbidity of the liquid determined at appropriate intervals. All results are ex-

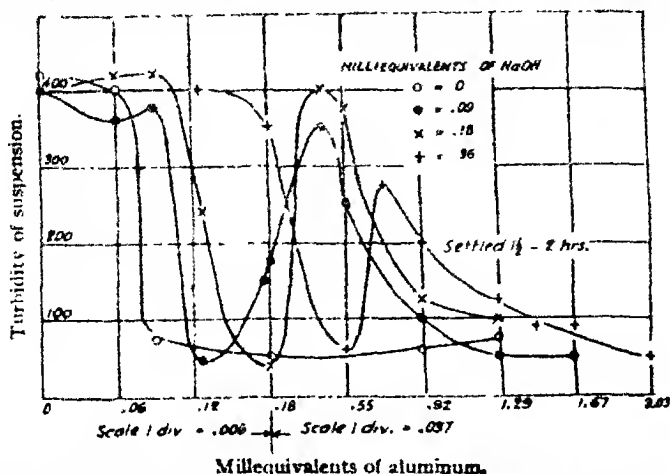


Fig. 4.—Effect of NaOH on the coagulation of a clay suspension by $\text{Al}_2(\text{SO}_4)_3$.

pressed as turbidities in parts per million and milligram equivalents per liter, except in the case of silicic acid, which is in parts per million of silica.

The action of salts on the coagulation of clay suspensions is shown in Figs. 2 and 3, and their action when the suspensions were coagulated by

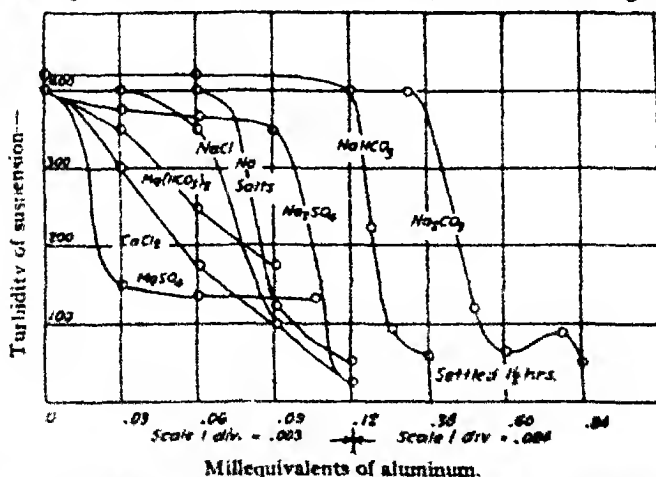


Fig. 5.—The effect of the addition of one milliequivalent of electrolytes on the coagulation of clay suspension by $\text{Al}_2(\text{SO}_4)_3$.

aluminum sulfate in Figs. 4, 5 and 6. These figures show in graphic form data from many experiments.

The salts arranged according to their efficiencies as coagulants are aluminum sulfate, calcium and barium hydroxides, calcium chloride, magnesium sulfate and magnesium and calcium hydrogen carbonates. The coagulative powers of calcium and barium hydroxides are practically the same and the ratio of aluminum to calcium and barium ions is about five to one. Sodium chloride has little effect until its concentration be-

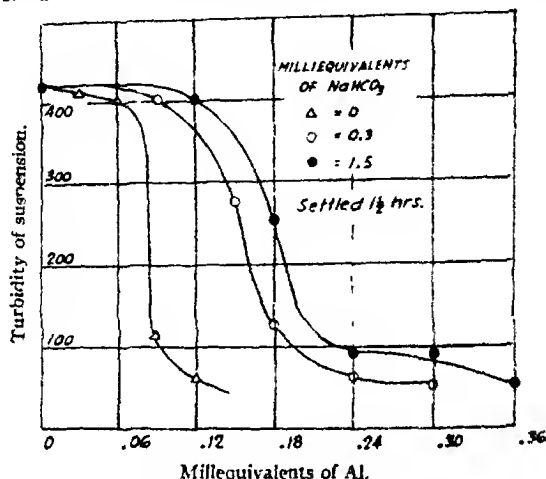


Fig. 6.—Effect of NaHCO_3 on the coagulation of clay suspension by $\text{Al}_2(\text{SO}_4)_3$.

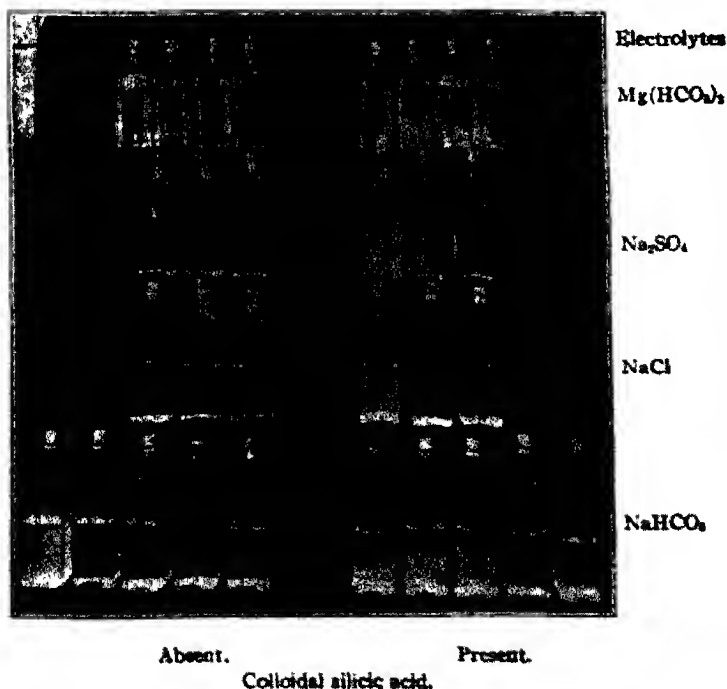
comes large. Sulfuric acid has no apparent effect up to a concentration of 0.35 millequivalents, but higher amounts coagulate the colloid. Sodium hydroxide, carbonate, acid carbonate and sulfate have at first a stabilizing influence followed by a coagulating effect, the hydroxide showing this action the greatest and the sulfate the least. The coagulating effect of anions seems to be an inverse function of their valences. since sodium sulfate disperses and sodium chloride does not

It is noticeable that this order is similar to that given above where the clay suspension was coagulated by the salt alone. Salts containing the bivalent cations, *i. e.*, calcium chloride, calcium hydrogen carbonate, magnesium sulfate and magnesium hydrogen carbonate, aid in the coagulation by alum and increase the rate of reaction; sodium chloride aids slightly; while sodium hydroxide, carbonate, hydrogen carbonate and sulfate prevent coagulation and retard the rate of reaction. In general, the magnitude of the effect is proportional to the concentration of the salts, but in the case of sodium hydroxide and carbonate, this is by no means true. With a given sodium hydroxide content and the addition of graded amounts of alum, there is first dispersion then coagulation, followed by a second disperse phase (not as stable as the first) and coagulation. See Fig. 7.

A third disperse state was not obtained by increase of alum or sodium hydroxide. As the content of sodium hydroxide is increased, additional amount of aluminum sulfate must be added in order to produce coagulation and to combat the dispersive action of the hydroxide or sodium compound. The concentration of chemicals necessary to produce coagulation does not vary with the alkalinity of the solution. Coagulation seems to be a function of the concentration of the hydroxyl ion and alkali metal ion as well as the cation and its valence. The monovalent ion of the alkalis in the presence of high hydroxyl ion concentration or *vice versa*, is intimately connected with dispersive or protective action in the coagulation of clay suspensions and probably with the peculiar (protective) effect of silicic acid in preventing the formation of aluminum hydroxide. If calcium is substituted for sodium these peculiar effects are not produced.

Effect of Silicic Acid on Coagulation.

The effect of silicic acid on the coagulation of clay suspensions by aluminum sulfate is in all cases to retard the reaction and more aluminum sulfate is required to coagulate than before, regardless of the presence or absence of electrolytes. This is shown in Tables II and III, and Fig. 7.



OTTO M. SMITH.

The photograph was taken 5 days after the addition of the aluminum sulfate; 62 parts per million of silicic acid (SiO_2) was added to the samples on the right.

The aluminum consumed is a function of the silicic acid added, but the mathematical relationship is not a simple one and varies with the clay used. This relationship is shown in Table II. In general, the amount of aluminum required to coagulate per unit amount of silicic acid added, is larger at low than at high concentrations. Silicic acid does not seem to stabilize or disperse the clay particles, as its presence does not influence the rate of sedimentation. In this respect it differs from the alkali salts.

Applications.

Removal of Silicic Acid from Water to be Used for Boiler Purposes. —

The experiments on natural waters indicate that silicic acid could be most economically removed by aluminum hydroxide formed in the reaction of aluminum sulfate with calcium hydroxide in a solution whose P_H value is 8.0 to 9.0 and that the precipitation is more or less directly related to the ratio of $(\text{Ca} + \text{Mg})/\text{Na}$. The higher this ratio the more complete is the removal. In one particular case by the proper treatment with aluminum sulfate and lime it was possible to reduce the silicic acid content from 82.6 to 30 parts per million with 6 grains per gallon of aluminum sulfate and the necessary amount of lime to soften.

TABLE II
Retarding Effect of Silicic Acid on the Coagulation of Clay Suspension by $\text{Al}_2(\text{SO}_4)_3$.
Silicic Acid (SiO_2) Added

Mg equivalents of Al	0 p p m		124 p p m		372 p p m	
	1 hr	24 hrs	1 hr	24 hrs	1 hr	24 hrs
0.03	400*	200				
0.09	175	5	150	100		
0.12	30	5	35	50	350	100
0.15			100	5	350	100
0.8			5	5	350	100
0.21			40	5	212	40
0.24			40	5	100	30
0.27					50	20

The Amount of $\text{Al}_2(\text{SO}_4)_3$ Necessary to Produce a Definite Clarification in One Hour in the Presence of Silicic Acid.

SiO_2 added P p m	$\text{Al}_2(\text{SO}_4)_3$ added to reduce turbidity to 50 p p m Mg. equivalents
0	0.115
12.4	0.200
24.8	0.240
37.2	0.270
49.6	0.330

* Turbidity of clay suspension.

TABLE III.
Retarding Effect of 62 p. p. m. Silicic Acid on the Coagulation of Clay Suspensions by $Al_2(SO_4)_3$ in the Presence of Electrolytes
Milligram Equivalents of Salts

Milli- equivalent of Al	¹ 5 NaHCO ₃		² NaCl		² Na ₂ SO ₄		² Mg(HCO ₃) ₂	
	Dialyzed Silicic Acid—p. p. m. as SiO ₂ .							
	0	62	0	62	0	62	62	62
0.03	.	.	35	350	400	400	400	400
0.06	400	400	.	350	.	400	400	400
0.07	.	.	350	325	75	400	.	.
0.12	.	.	.	32	.	350	350	350
0.15	25	25	.	.
0.18	400	400	35	125	.	.	300	300
0.21	10	10	.	.
0.30	5	400	35	15
0.30	65	350
0.60	65	300

Readings expressed as turbidity. Time, 3 hours

The Coagulation of Waters Containing Colloidal Clay.—The stability of a suspension of clay seems to be intimately and directly connected with amount of monovalent cations and bivalent anions present. Thus the alum needed to coagulate will be greater the larger the concentration of sodium ions except in the case when the anion is mainly chlorine. Less alum will be needed as the ratio of the calcium and magnesium ions to the sodium ion increases. As the silicic acid content increases more alum will be required to coagulate. In concentrations up to 20 parts per million, from 0.015 to 0.03 milligram equivalents of aluminum per 10 parts of silica is needed to cancel the influence of the silicic acid.

Water containing bivalent ions when treated with alum gives a sharp abrupt reaction, an increase of 0.03 milligram equivalents of aluminum coagulates but when silicic acid or alkalies are present, other factors being constant, a much larger amount of alum is necessary to produce the same clarification and the abruptness of the reaction becomes less as the amount of the silicic acid and alkalies approaches a certain maximum where the magnitude of the change produced per unit amount of alum is much smaller than in the former case (see Fig. 6). This phenomenon is exactly similar to that which occurs when "colloidal waters" are coagulated by alum and lime.

These experiments justify the addition of an excess of calcium hydroxide and allowing it to react with the water for some time (8 to 12 hours) before the addition of the alum or ferrous sulfate. This procedure has been effective in purification of water from the Arkansas River at Little Rock, Arkansas, where the suspended material is in a colloidal state and consists largely of a very finely dispersed clay in a concentration of 200 to 400 p. p. m.

Summary.

1. Dilute solutions of dialyzed and undialyzed silicic acid behave towards electrolytes in the same manner as concentrated solution with the exception that proportionally more reagent is needed.
2. The optimum hydrogen ion concentration for the precipitation of the aluminum hydroxide and the removal of silicic acid by aluminum hydroxide is a concentration of 1×10^{-8} .
3. The limiting values of the hydrogen ion concentration, between which the solid aluminum hydroxide phase is present, are 1×10^{-4} and 1×10^{-11} .
4. The presence of silicic acid prevents the formation of a precipitate of aluminum hydroxide, when the sodium hydroxide, equivalent to the aluminum chloride present, is added all at once. The silicic acid probably acts as a protective colloid preventing precipitation of the aluminum hydroxide. The presence of bivalent cations destroys this protective power.
5. The action of electrolytes on clay suspensions is the same in dilute as in concentrated suspensions.
6. Sodium hydroxide, hydrogen carbonate, carbonate and sulfate stabilize or disperse clay suspensions at one concentration and coagulate at another.
7. The ratio of the coagulating power of calcium and barium hydroxides to aluminum hydroxide is about 1 to 5.
8. Coagulation of clay suspensions is aided by the bivalent and hindered by monovalent cations in the presence of acid carbonate, carbonate, sulfate and hydroxyl anions.
9. Silicic acid retards coagulation of clay suspensions.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MT. UNION COLLEGE.]

A SURFACE TENSIMETER FOR SMALL QUANTITIES OF LIQUIDS.

By C. C. KIPLINGER

Received November 12 1919

An instrument for measuring surface tension which requires only a drop or two of the liquid under examination has been developed in our laboratories as an aid in the identification of organic liquids. It comprises a piece of capillary glass tubing 18 cm. long, about 1 mm. internal and 4 mm. external diameter. This is broken very carefully from a long piece by making a minute cut in the glass with a carborundum crystal, then breaking as usual, using all possible precautions to get a clean cut and a right-angled fracture. Several tubes should be broken and the

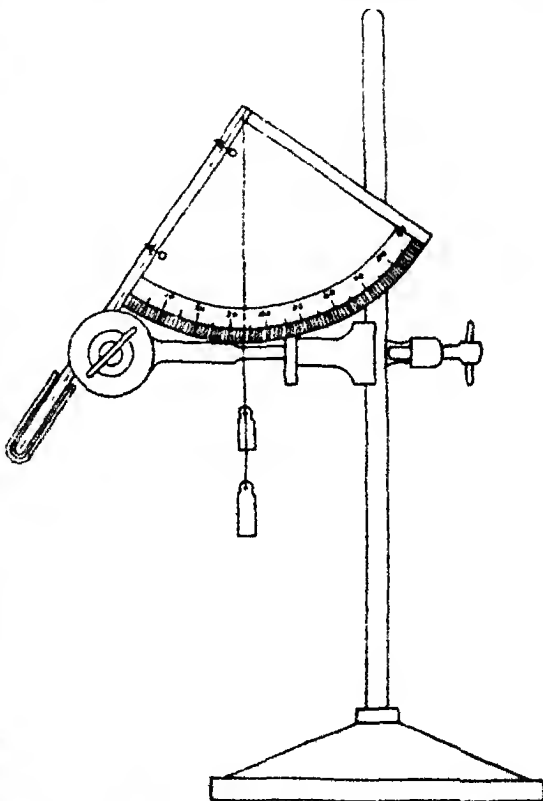
best one selected for this purpose. A quadrant cut from a celluloid protractor is pierced with two holes and attached to the tube with the device previously described,¹ so that it may be removed with ease or adjusted to tubes of different diameters.

A small notch cut in the apex of the quadrant holds a thread in position which passes over it, the thread carrying a small weight at each end and serving to indicate the angular displacement of the tube. The threads on each side of the protractor eliminate the error of parallax in the readings. A perforated cork supporting a bolt and two grooved cork washers is held by a clamp and stand and carries the tube and its attachments. A glass cap 5 cm. long made from a bit of tubing large enough to pass over the capillary tube without binding, serves to retard evaporation.

The tube is thoroughly cleaned and dried and a short column of liquid, 1 cm. to 3 cm. (the lower the tension and the greater the density, the shorter the column) introduced into the capillary. The tube with its enclosed thread of liquid is then turned to such an angle that the meniscus at the lower end changes to a plane surface. The point at which this occurs is observed by the use of a pocket magnifier. This adjustment should be made in a good light with a sheet of white paper as a background. The angle A is then read and checked by readjusting 2 or 3 times and the length L of the liquid thread measured to 0.1 mm.

$L \cos A = h$, where h is the height of the vertical column exerting the same downward pressure as the inclined thread of liquid. The tube may

¹ *J. Ind. Eng. Chem.*, 10, 8, 631 (1918).



be calibrated with water and the true diameter of the capillary thus determined, or this diameter may be measured directly with a microscope and micrometer. The latter method was used in this work.

The familiar formula $T = \frac{d \times h \times r \times 980}{2}$ dynes per cm. is used in the calculation of T , the surface tension.

Experimental Results.

Water, benzene, toluene, carbon tetrachloride, and ethylene dibromide were purified according to directions given in part by Richards and Coombs,¹ and the temperature coefficients were taken from a paper by Harkins,² which also gives the surface-tension constants for more than 300 substances.

The water used was redistilled from potassium permanganate and sulfuric acid, boiled in a quartz vessel just before using and the capillary filled with the hot liquid, then allowed to stand until coming to room temperature.

TABLE I.—RESULTS OBTAINED BY USING A POCKET MAGNIFIER

Angle of inclination measured from horizontal therefore $A = 90^\circ$ —angle			Correct value
Expt	Water, degrees	T_{20° Dynes cm.	
1.....	56 5	71 1	
2.....	65 5	70 7	
3.....	58	71 8	
Av., 71 2			72.7
Benzene			
1.....	53 5	25 9	
2.....	56 5	26 4	
3.....	42 5	27 4	
Av., 26 6			28.9
Carbon Tetrachloride			
1.....	28 5	23 9	
2.....	58	23 8	
3.....	61 5	23 7	
4.....	44 5	24 7	
Av., 24 0			26.7

From the above results it is apparent that this method will serve to distinguish between liquids, the surface tensions of which show a difference of 2 or 3 units. The experimental results are generally low, the above figures being typical. The variations in readings are due in part to the difficulty experienced in determining the exact position in which the meniscus changes to a plane surface. Moreover, it is a hard matter to adjust and read the instrument for angles greater than 70° , hence

¹ THIS JOURNAL, 37, 1656-76 (1915).

² *Ibid.*, 39, 556-69 (1917).

the used angles lie chiefly between 50° and 70° . However, there seems to be little change in accuracy for different angular readings.

The results are very much improved by attaching the tensimeter to the stage of a compound microscope and obtaining the angles by tilting the body of the microscope. The cap of the tensimeter was taped to a rather thick glass slide and proved an adequate support for the capillary tube and quadrant, allowing it to be easily removed. The stage springs

TABLE II—RESULTS OBTAINED BY USING A MICROSCOPE.

Expt	Angle, degrees $A = 90^\circ - \text{angle}$	120° Dynes, cm Water	Correct value.	Error, %
1	59	71.6		
2	62.5	72.2		
3	64.5	71.2		
4	68.5	71.5		
5	54	71.1		
		—		
		Average, 71.6	72.7	-1.5
		Benzene.		
1	56	27.7		
2	65	28.5		
3	49	26.8		
4	65.5	27.3		
5	63.5	27.4		
		—		
		Average, 27.5	28.0	-4.8
		Carbon Tetrachloride.		
1	63	25.2		
2	71	24.3		
3	50	25.7		
4	55	26.8		
5	50.5	25.4		
		—		
		Average, 25.5	26.7	-4.5
		Toluene.		
1	65.5	26.5		
2	51.25	27.1		
3	55.75	27.4		
4	69.5	27.0		
5	55	27.0		
		—		
		Average, 27.2	28.58	-4.8
		Ethylene Dibromide		
1	49.25	37.7		
2	50	37.2		
3	52.75	37.5		
4	58.5	37.7		
5	45	37.7		
		—		

held the slide firmly enough to prevent movement of the assembled apparatus. The results given above were obtained with a 10X micrometer eyepiece and a $\frac{2}{8}$ in. objective. The microscope was first focussed on the upper edge of the tube, the position of which was read on the micrometer scale, then focussed down to the bottom of the meniscus, which should be so illuminated as to show as a bright line, and the body inclined until the upper edge of the bright line broadened and touched the scale mark, which from the first reading indicated the position of the upper edge of the tube. If a micrometer eyepiece is not available, one with cross-hairs will serve to locate the edge of the tube, although the difficulty of adjustment is somewhat increased. It is obvious that tubes with their ends ground accurately at right angles and polished would give better results than those used in this work. The determinations can be made very rapidly.

The fact that these results are uniformly low is striking. This may be due in part to a slight change in the length of the column arising from the flattening of the meniscus, the actual length being slightly greater than the distance as measured between the bottoms of the two menisci. A correction factor is indicated.

The writer is indebted to Dr. W. B. Harkins for his kind suggestions relative to the testing of this instrument.

Summary.

A device is described, by means of which the surface tension of a liquid may be determined when only a drop or two is available, and which may be used as an aid in identifying organic liquids.

ALLIANCE, OHIO

(CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF
THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY NO 120)

A THERMODYNAMIC INVESTIGATION OF REACTIONS INVOLVING SILVER SULFIDE AND SILVER IODIDE.

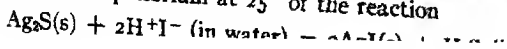
By ARTHUR A. NOYES AND E. STANLEY FREED

Received November 29, 1919

CONTENTS 1 Outline of the Investigation 2 Description of the Equilibrium Experiments 3 The Data of the Equilibrium Measurements and the Activity-Coefficients Calculated from Them 4 Discussion of the Activity Coefficients Derived from the Equilibrium Measurements. 5 The Electromotive Force of Hydrogen Silver-Sulfide Cells 6 The Electromotive Force of Hydrogen Silver-Iodide Cells. 7 Free-Energy Changes Attending the Reactions. 8 Summary of the Free-Energy Values.

1. Outline of the Investigation.

This research consists on the experimental side primarily in a determination of the equilibrium at 25° of the reaction



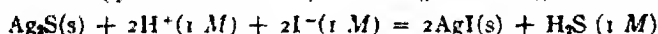
It was undertaken with two distinct objects in view. The first of these objects was to determine how the activity coefficient (or effective ionization) of the acid varies with its concentration. The second object was to determine the free-energy change attending the reaction.

This reaction is especially well adapted for determining the variation of the activity coefficient α of hydriodic acid with its concentration c , in the respect that a small change in the ion-concentration $c\alpha$ causes a very much larger change in the hydrogen sulfide concentration, as will be seen from the mass-action expression

$$K = (\text{H}_2\text{S})/(\text{H}^+)^2(\text{I}^-)^2 = (\text{H}_2\text{S})/(c\alpha)^4.$$

This fact carries with it, however, the disadvantage that the study can be extended over only a small range of acid concentration. Thus our experiments had to be confined to concentrations of hydriodic acid between 0.024 to 0.116 normal.

The free-energy decrease ($-\Delta F$) attending the change in state



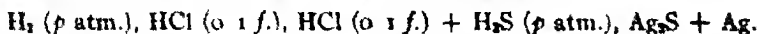
can be computed by the familiar thermodynamic equation

$$-\Delta F = RT \log K,$$

using the equilibrium constant K derived from the experiments and making the most reasonable assumption as to the ionization. By combining with this free-energy decrease the previously determined free energies of silver iodide and of hydrogen iodide in dilute solution we may derive the free-energy change attending the reaction



To confirm these results these free energies were also determined by measuring the electromotive force at 25° of the cells



Finally, to determine the heat effect attending the reaction, the electromotive force of the first of these cells was measured at other temperatures.

2. Description of the Equilibrium Experiments.

The substances used in the experiments were prepared as follows: The water was redistilled from alkaline permanganate, rejecting the first fourth of the distillate. The hydrogen sulfide was made by treating ferrous sulfide with hydrochloric acid and washing the gas with a small quantity of barium hydroxide solution. The silver iodide was prepared by adding hydriodic acid solution to an excess of silver nitrate solution and thoroughly washing the precipitate by decantation in blackened bottles. The hydriodic acid solution was made from iodine sublimed from a mixture of it with potassium iodide and then resublimed alone.

This iodine was added to water, and hydrogen sulfide was passed in, the liquid being decanted from the sulfur after several days and filtered through an alundum filter. It was kept under an atmosphere of hydrogen sulfide.

The equilibrium mixtures were prepared as follows: To the silver iodide in blackened bottles hydriodic acid of various concentrations was added. A rubber stopper carrying 3 glass tubes, each with a glass stopcock, was then inserted in the neck of each bottle. Two of these tubes extended beneath the liquid in the bottles. One of these served to pass hydrogen sulfide into the mixture; and the other, provided with an alundum filter, to withdraw samples of the solution for analysis. The third tube extended only into the gas space above the liquid and served to regulate the gas pressure inside the bottles. Hydrogen sulfide was then passed into the mixture until the silver iodide began to darken. To approach the equilibrium from the opposite side hydriodic acid was added to mixtures already approximately at equilibrium. The necks of the bottles and the protruding tubes were well coated with paraffin to prevent leakage. The bottles were placed on a horizontal shaft in a thermostat at 25° and rotated for several days.

The bottles were then hung upright in the thermostat and the solid allowed to settle. Two samples of the solution were withdrawn, one for the determination of the hydrogen sulfide, the other for that of the hydriodic acid, at the same time nitrogen being allowed to draw into the bottle. The first sample was caused to suck up into an evacuated weighed bulb containing a known quantity of iodine dissolved in potassium iodide solution; whereupon the bulb was reweighed and the excess of iodine unconsumed by the hydrogen sulfide was titrated with standard sodium thiosulfate solution with the aid of starch or (in case of the more dilute solutions) of carbon disulfide. The other sample, consisting of about 15 cc., was weighed, diluted with 75 cc. of water, boiled to expel the hydrogen sulfide, and titrated with standard sodium hydroxide solution with the aid of phenolphthalein. These analytical methods were tested in advance and found to give results accurate within 0.2%.

3. The Data of the Equilibrium Measurements and the Activity Coefficients Calculated from Them.

In the following table is given in the first column the number of the experiment; in the second column, the number of days the mixture was rotated; in the third column, a letter *l* or *r* showing whether the equilibrium was being approached from the left or right hand side of the reaction $\text{Ag}_2\text{S} + 2\text{HI} = 2\text{AgI} + \text{H}_2\text{S}$; in the fourth and fifth columns, the concentrations c_{HI} and $c_{\text{H}_2\text{S}}$, expressed in formula weights per liter, of the hydriodic acid and hydrogen sulfide in the equilibrium mixtures; in the sixth column, the equilibrium constants K calculated from them.

by the equation $K = c_{\text{H}_2\text{S}}/(c_{\text{HI}}\gamma)^4$ with the aid of values of the ionization γ given in the seventh column derived from the equivalent conductance measurements of Strachan and Chu;¹ and in the eighth column the values of the activity coefficient α of the hydriodic acid calculated by the equation $\alpha = \gamma(K)^{0.25}/5.558$, which is derived from the theoretical expression $c_{\text{H}_2\text{S}}/(c_{\text{HI}}\alpha)^4 = \text{const.}$, under the arbitrary assumption that at 0.025 *N* (where $K^{0.25} = 5.558$) the activity coefficient α and the ionization γ have the same value, 0.924.

TABLE I.—THE EQUILIBRIUM DATA AND THE EQUILIBRIUM CONSTANTS AND ACTIVITY COEFFICIENTS CALCULATED FROM THEM

Expt	Days rotation	Direction	Concentration		Equilibrium constant <i>K</i>	Ionization γ	Activity coefficient α
			HI_2	HI			
1	7	<i>r</i>	0.0002522	0.02426	906	0.924	0.935
2	7	<i>r</i>	0.0002944	0.02580	915	0.923	0.914
3	7	<i>r</i>	0.0003424	0.02655	951	0.923	0.922
4	3	<i>l</i>	0.001002	0.03478	966	0.918	0.920
5	3	<i>l</i>	0.002807	0.04526	991	0.912	0.918
6	7	<i>r</i>	0.004058	0.05023	932	0.910	0.905
7	3	<i>l</i>	0.005029	0.05282	968	0.909	0.912
8	7	<i>r</i>	0.006801	0.05678	967	0.907	0.910
9	2	<i>l</i>	0.01071	0.07450	974	0.906	0.905
10	2	<i>l</i>	0.03298	0.08506	974	0.897	0.902
11	2	<i>l</i>	0.03349	0.08551	969	0.896	0.900
12	3	<i>l</i>	0.06330	0.1008	971	0.892	0.896
13	3	<i>l</i>	0.07695	0.1061	966	0.890	0.893
14	3	<i>l</i>	0.1108	0.1162	973	0.889	0.893
Mean					964		

4. Discussion of the Activity Coefficients Derived from the Equilibrium Measurements.

In the first place, the fact may be pointed out that there is no regular difference between the equilibrium constants obtained in approaching the equilibrium in the two opposite directions, showing that equilibrium was in reality attained.

Next it may be noted that the equilibrium constants exhibit only a very slight variation with the concentration, and that correspondingly the activity coefficients change with the concentration at nearly the same rate as the ionization values derived from the conductance ratios. It is to be remembered, however, that the range of concentration here involved (0.025 to about 0.12 formal) is relatively small, and that this may not be true in general.

Finally, the results may be compared with those obtained for hydrochloric acid by Noyes and Ellis.² Between the concentrations 0.025

¹ THIS JOURNAL, 36, 818 (1914).

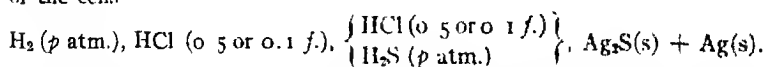
² ILL. EN. 2025 (1914).

and 0.12 the activity coefficient of hydrochloric acid decreases 8.3%, while that of hydriodic acid decreases only 4.5%.

It is to be noted that these values of the activity coefficient are only relative, as they are based on the arbitrary assumption that the value is identical with that of the ionization at 0.025 formal, and that, for example, values 3.8% smaller result if the activity coefficient be taken as identical with that of hydrochloric acid at 0.025 formal, for which 0.889 was found by Noyes and Ellis (instead of 0.924).

5. The Electromotive Force of Hydrogen Silver-Sulfide Cells.

We determined the electromotive forces at 5° or 10°, at 25°, and at 35°, of the cells



The apparatus used consisted of 2 tubes connected by a siphon provided with a stopcock. Two separate platinized-platinum electrodes, prepared by M. Chow, of this laboratory, as described by Ellis,¹ were placed in one tube, and electrolytic hydrogen was continuously bubbled through it. This hydrogen was washed with alkaline pyrogallate and acid potassium dichromate; and, before entering the cell, it was passed through a bulb containing hydrochloric acid of the same strength as was present in the cell and having the same temperature. Four separate silver sulfide electrodes were placed in the other tube. These were made by coating silver-plated platinum spirals with a paste of silver oxide, and heating them until the oxide was decomposed, leaving a rough pure white mass of metallic silver. In case of the cell with the 0.1 formal acid the electrodes were dipped in a hydrogen sulfide solution, thus covering them with a thin coat of silver sulfide. In the cell with 0.5 formal acid they were previously coated with silver iodide, and later the iodide was converted to sulfide with a hydrogen sulfide solution. Solid silver sulfide, prepared by passing hydrogen sulfide into a silver nitrate solution and thoroughly washing the precipitate, was added to the acid solution in the tube containing the silver-sulfide electrodes. Through the tube containing these electrodes hydrogen sulfide was slowly bubbled. This hydrogen sulfide was made by heating a magnesium hydrosulfide solution prepared by passing ordinary hydrogen sulfide (made from ferrous sulfide and hydrochloric acid) into a cold suspension in water of carbonate-free magnesium oxide. In this way with 300 g. of magnesium oxide there could be obtained for many hours a steady stream of hydrogen sulfide easily controllable by the amount of heat applied.

The hydrogen and hydrogen sulfide gases both escaped at atmospheric pressure. Their partial pressures were, therefore, less than that of the

atmosphere by the vapor pressure of water in the hydrochloric acid solution at the temperature of the measurement. They were equal to each other and consequently the electromotive force was independent of the pressure.

The observed data are given in the following table. The first and second columns show the temperature and concentration in formula weights of per liter of solution. The third gives the number of hours that elapsed between the setting up of the cell and the first measurements. In the fourth column is recorded the mean result of these first measurements, this mean being the average of the 8 observations made with the 8 different combinations of the 2 hydrogen electrodes and the 4 silver sulfide electrodes. In the fifth and sixth columns are given the corresponding mean results obtained one hour and two hours later than the first measurement. The seventh column shows the average deviation from the mean result of the 8 observations from which it was derived.

TABLE II--THE OBSERVED ELECTROMOTIVE FORCES OF THE HYDROGEN SILVER-SULFIDE CELLS

Temp. °	Formal acid conc.	Elapsed time in hours	Observed electromotive forces			Average deviation
25	0.1	13	+0.03670	+0.03669	-0.03670	0.00003
15	0.1	3	+0.03586	+0.03582	-0.03584	0.00004
10	0.1	3	+0.03781	+0.03779		0.00003
35	0.5	6	+0.03560	+0.03559	-0.03570	0.00003
5	0.5	1	+0.03794	+0.03794	-0.03791	0.00013
35	0.5	4	+0.03583	+0.03574	-0.03572	0.00003

The following table contains the mean values derived from the foregoing observations for the cells formulated at the beginning of this section, together with values (within parentheses) interpolated for the temperatures at which measurements were not made:

TABLE III MEAN VALUES OF THE ELECTROMOTIVE FORCE OF THE HYDROGEN SILVER-SULFIDE CELLS

Temp. °	Cell with		Final value
	0.1 <i>N</i> HCl	0.5 <i>N</i> HCl	
5	(-0.0318)	-0.0303	-0.03805
10	-0.03779	(-0.03756)	-0.03767
25	-0.03670	(-0.03645)	-0.03638
35	-0.03584	-0.03571	-0.0357

Reversing the sign of the numbers given in the last column of the table, we get the values of the specific electrode potential

$$\left\{ \begin{array}{l} \text{Ag} \\ \text{Ag}_2\text{S} \end{array} \right\}, \left\{ \begin{array}{l} \text{H}_2\text{S (1 atm.)} \\ \text{H}^+ (1 M) \end{array} \right\}.$$

6. The Electromotive Force of Hydrogen Silver-Iodide Cells.

The cells studied were H_2 (*p* atm.), HI (0.030 or 0.098 *f*.), $\text{AgI} + \text{Ag}$.

sulfide cells. The silver silver-iodide electrodes were prepared in several ways. The first ones (denoted by A in the table below) were made by dipping silver silver-sulfide electrodes into a hydrogen iodide solution. Others (denoted by B) were made by electrolyzing silver-iodide on to the electrodes A just described with a current of 0.002 ampere for 2 hours. The final electrodes (denoted by C) were made by pasting precipitated silver-iodide on to these electrodes B, and heating them for 2 hours at a temperature of 120° to convert any amorphous silver iodide to the crystalline state. The pressure of the hydrogen was always equal to the barometric pressure diminished by the vapor pressure of water in the solution.

The observed data are given in Table IV. The first and second columns show the temperature and the concentration in formula weights of hydrogen iodide per liter of solution. The third column contains letters representing the electrodes prepared in the different ways indicated above. The fourth column gives the number of hours that elapsed between the setting up of the cell and the first constant measurements; and the fifth shows the barometer reading at the time of these measurements. In the sixth and seventh columns are recorded the mean results of these electromotive-force measurements and the average deviations of the 8 observations made with the 8 different combinations of the 2 hydrogen electrodes and the 4 silver silver iodide electrodes. In the eighth column are given these electromotive forces corrected to a hydrogen pressure of one atmosphere. In the last column, headed Specific E. M. F., is given the electromotive force of the cell H_2 (1 atm.), H^+ (1 M.) || I^- (1 M.), $\text{AgI} + \text{Ag}$, as calculated from the electromotive forces in the eighth column by the logarithmic formula with the aid of the activity coefficients (0.921 and 0.897) for 0.0300 and 0.0980 formal hydrogen iodide solutions, obtained by interpolation from the values given in Table I. These last values with sign reversed are the values of the specific electrode potential $\text{Ag} + \text{AgI}, \text{I}^-$ (1 M.)

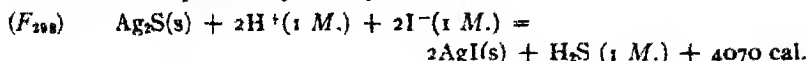
TABLE IV.—THE ELECTROMOTIVE FORCES OF THE HYDROGEN SILVER-IODIDE CELLS.

Temp	HI conc	Electrodes	Elapsed Time Hrs	Bar press	Observed E M F	Av dev	Corrected E M F	Specific E M F
25	0.0980	A	2	756	—0.02329	0.00002	—0.02282	—0.14775
2	0.0980	B	4	766	—0.02326	0.00007	—0.02297	—0.14790
25	0.0980	C	10	753	—0.02336	0.00008	—0.02285	—0.14778
25	0.0300	C	6	761	+0.03640	0.00014	+0.03678	—0.14764
25	0.0300	C	7	761	+0.03645	0.00018	+0.03683	—0.14759
Mean,								—0.14773

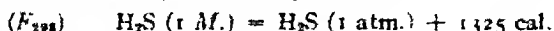
7. Free-Energy Changes Attending the Reactions.

The free-energy decrease attending the reaction whose equilibrium we studied is found by the equation

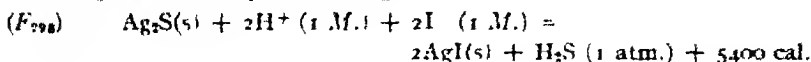
(adopting the mean value of K given in Table I) to be 4070 cal. at 25°. This result is expressed by the equation¹



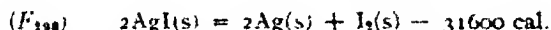
From Pollitzer's² determination that the solubility of hydrogen sulfide at 25° is 0.1004 molal when its partial pressure is 737 mm. we find with the aid of the usual logarithmic expression



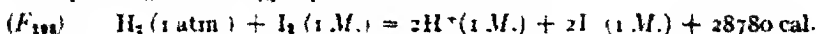
Adding these two equations we get.



Jones and Hartman³ found that the electromotive force at 25° of the cells $\text{Ag} + \text{AgI}, \text{KI} (0.05f. \text{ and } 0.1f.), \text{I}_2(s)$, after correcting for the triiodide concentration at the iodine electrode and for the liquid potential arising from it, is +0.6847 volt. This corresponds to the following equation.



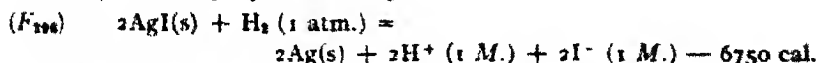
Lewis and Randall⁴ have reviewed the data on the electrode potential of iodine, and on the basis of the measurements of Farragher find for the cell $\text{I}_2(1 M.), \text{I}^-(1 M.) \parallel \text{KCl}(0.1 N), \text{KCl}(1 N), \text{Hg}_2\text{Cl}_2 + \text{Hg}$ at 25° the value -0.3407 volt. Adding to this the value -0.2828 volt recently derived by Lewis, Brighton and Sebastian⁵ for the cell $\text{Hg} + \text{Hg}_2\text{Cl}_2, \text{KCl}(1 N), \text{KCl}(0.1 N) \parallel \text{H}^+(1 M.), \text{H}_2(1 \text{ atm.})$ at 25°, we get for the cell $\text{I}_2(1 M.), \text{I}^-(1 M.) \parallel \text{H}^+(1 M.), \text{H}_2(1 \text{ atm.})$, or for the electrode potential of dissolved iodine, the value -0.6235 volt. The corresponding free-energy equation is



Lewis and Randall⁶ have also derived the equation



Adding the last 3 equations we get



Adding this equation to the one preceding the last 3 equations we get

¹ Throughout this article the symbols F_{xxx} and H_{xxx} prefixed to equations indicate that they are free-energy equations or heat-content equations, respectively, and that they refer to 25° C. or 298° A. In general, the conventions employed are those adopted by Lewis (THIS JOURNAL, 35, 1-30 (1913); 36, 1969-1993 (1914)).

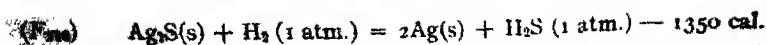
² Z. anorg. Chem., 64, 121 (1909).

³ THIS JOURNAL, 37, 752 (1915).

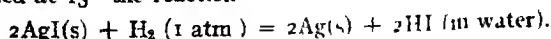
⁴ Ibid., 36, 2264 (1914).

⁵ Ibid., 39, 2259 (1917).

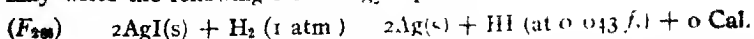
⁶ Ibid., 36, 2262 (1914).



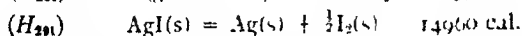
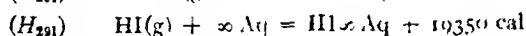
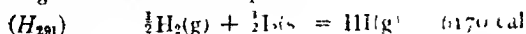
We may derive other values of the free-energy decrease attending these reactions with the aid of the equilibrium measurements of Danneel,¹ who studied at 13° the reaction



Danneel approached the equilibrium from both sides, using platinum black as a catalyzer, and found the equilibrium concentration of the hydrogen iodide to be 0.0430 formal. Since, when the change takes place under equilibrium conditions, the free energy change is zero, we may write the following free energy equation

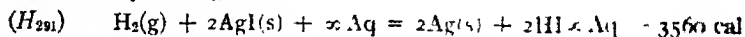


To calculate the free-energy change at 25° we need the value of the heat content attending the reaction. This is obtained by combining the following thermochemical equations



Thomsen² and Berthelot³ measured the first and second of these reactions with fairly concordant results (6040 and 6300, 19200 and 19500). For the heat of formation of 1 AgI(s) the best values are evidently those (14820 and 15100 cal.) recently determined by Fischer⁴ and Braune and Koref.⁵ The means of these values have been adopted in the foregoing equations

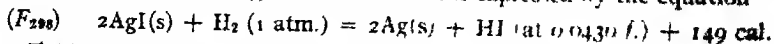
Adding together these 3 thermochemical equations and multiplying the result by 2 we get



Substituting in the general free energy equation

$$\frac{(-\Delta F_2)}{T_2} - \frac{(-\Delta F_1)}{T_1} = \Delta H \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

for ΔH the value -3560 and for $-\Delta F$, the value 0 at $T_1 = 286$, we find that at 25° ($T_2 = 298$) the free-energy decrease $-\Delta F$, for the same change in state has the value 149 cal. This result is expressed by the equation



Taking the activity coefficient of 0.043 f. hydrogen iodide as 0.918, as given in Table I, we derive from the preceding equation by the usual logarithmic formula the following

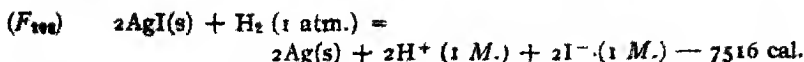
¹ *Z. phys. Chem.*, 33, 429 (1900).

² *J. prakt. Chem.*, [2] 12, 289 (1875), "Thermochemische Untersuchungen," 3, p. 380.

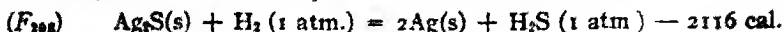
³ *Ann. chim. phys.*, [5] 29, 243 (1884) Berthelot's "Thermochemie," 2, 370 (1897).

⁴ *Z. anorg. Chem.*, 78, 41 (1912).

⁵ *Ibid.*, 87, 185 (1914).

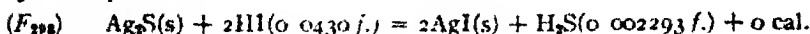


Adding this to the third equation in this Section we get

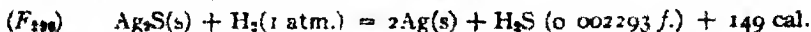


We may also derive the free-energy change attending this last reaction from the equilibrium measurements of Danneel and of ourselves, without making any assumption as to the activity coefficient, as follows:

We find by interpolation that the concentration of hydrogen sulfide which is in equilibrium with a 0.0430 formal hydrogen iodide solution when silver-iodide and -sulfide are also present is 0.002293 formal. At these concentrations the free-energy decrease will be zero, as expressed by the equation



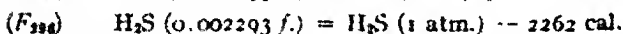
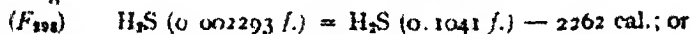
Adding the two preceding equations we get



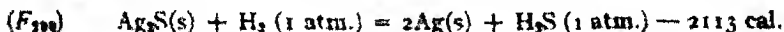
Now the data of Pollitzer¹ shows that, when the partial pressure of the hydrogen sulfide is one atmosphere, the concentration of hydrogen sulfide in 0.0430 formal hydrogen iodide solution is 0.1041 formal. From the relation

$$-\Delta F = RT \log_e \frac{0.002293}{0.1041},$$

we get

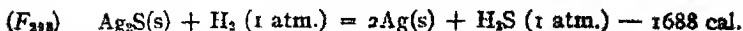
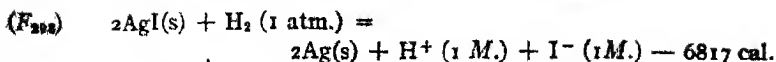


By combining the last of these two equations with the one preceding them, we get

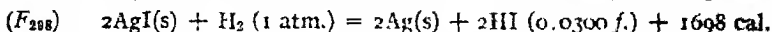
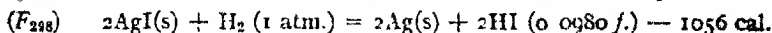


Finally, we may derive directly from the electromotive-force measurements given in Tables III and IV the free-energy decrease attending the two main reactions under consideration. Namely, multiplying the electromotive forces (-0.14773 and -0.03658 volt) of the hydrogen silver-iodide cell and of the hydrogen silver-sulfide cell at 25° by 193,000 and dividing by 4.182, we find the result expressed by the following equations:

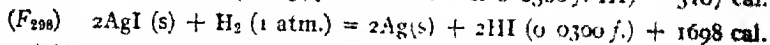
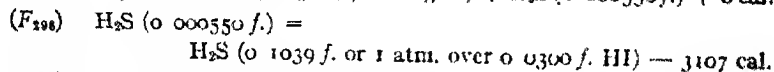
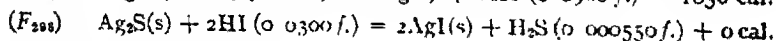
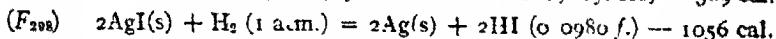
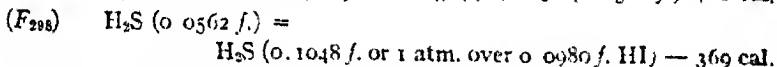
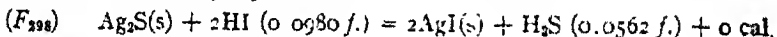
¹ *Z. anorg. Chem.*, 64, 121 (1900). By plotting Pollitzer's values of the solubility of hydrogen sulfide in hydrogen iodide solutions, when the total pressure of the gas is one atmosphere, against the concentration of the hydrogen iodide, the equation of the most representative straight line through the points is found to be $c_{\text{H}_2\text{S}} = 0.1004 + 0.01248c_{\text{HI}}$. This gives for the value of $c_{\text{H}_2\text{S}}$ when c_{HI} is 0.043 formal the value 0.10094 formal. This refers, however, to a partial pressure of the hydrogen sulfide of 737 mm., the vapor pressure of the water in the 0.043 f. HI solution being 23 mm. Hence, for a partial pressure of one atmosphere, $c_{\text{H}_2\text{S}} = 0.10094 \times 760/737 = 0.1041$ formal.



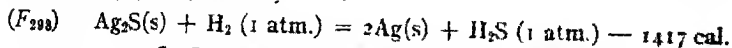
For the last of these reactions we can derive another value from the electromotive forces of the hydrogen silver-iodide cell (without using the activity coefficient of hydriodic acid) by combining them with the results of our equilibrium measurements. Namely, multiplying the electromotive forces (-0.02288 and $+0.03680$ volt) of the cells with 0.0980 and 0.0300 formal hydrogen iodide solutions by $193,000$ and dividing by 4.182 we get the results expressed by the two following equations:



Now we find from our equilibrium measurements by interpolation that with 0.0980 formal hydrogen iodide the corresponding hydrogen sulfide concentration is 0.0562 formal, and that with 0.0300 formal hydrogen iodide the hydrogen sulfide concentration is 0.000550 formal. And by treating these results as we did those of Danneel, we get the following two groups of free-energy equations:



Adding the equations in each of these two groups, we get for the free-energy decrease -1425 and -1409 cal., respectively. Adopting the mean (-1417 cal.) we may write



8. Summary of the Free-Energy Values.

The results of the preceding calculations may be summarized as follows:

We have found for the free-energy decrease attending the reaction $2\text{AgI(s)} + \text{H}_2 (1 \text{ atm.}) = 2\text{Ag(s)} + 2\text{H}^+ (1 M.) + 2\text{I}^- (1 M.)$ at 25° the following values:

(a) -6750 cal. from the e. m. f. data of Jones and Hartman on iodine silver-iodide cells and the electrode-potential calculations of Lewis and Randall relating to hydrogen iodide.

(b) -6817 cal. from our e. m. f. data on hydrogen silver-iodide cells.

(c) —7516 cal. from the measurements of Danneel on the equilibrium of the reaction at 13°, and the available thermochemical data.

We have found for the free-energy decrease attending the reaction



the following values:

(d) —1350 cal. from our equilibrium results and result (a) above.

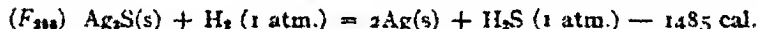
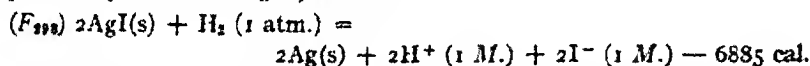
(e) —1417 cal. from our equilibrium results (b) above.

(f) —1688 cal. from our e. m. f. data on hydrogen silver-sulfide cells.

(g) —2116 cal. from our equilibrium results and result (c) above.

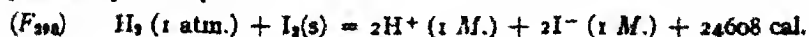
(h) —2113 cal. from our equilibrium results and those of Danneel directly.

It will be seen that the results (c), (g), and (h), which involve Danneel's equilibrium measurements, are much larger numerically than results (a) and (b) and results (d), (e), and (f), which are based on the electromotive force data. As the latter results are fairly concordant and come from 2 or from 3 independent series of electromotive force measurements, it seems best to adopt as final values the averages of these results, which are expressed by the following equations:

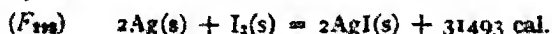


We have attempted to formulate a temperature function that would bring this last free energy value into relation with those determined by Keyes and Felsing¹ for the same reaction at 470–630°, but have become convinced that the values of the heats of reaction and of the heat capacities available at present are not accurate enough to enable this to be done satisfactorily.

By combining the first of the last two equations with the free energy of formation of iodide ion, as determined by Lewis and Randall² and expressed by the equation



we get the equation



Half this quantity, or 15750 cal., is the free-energy decrease attending the formation of one AgI(s) from its elements at 25°.

CAMBRIDGE, MASS.

¹ THIS JOURNAL, 42, 246, 251 (1910).

² *Ibid.*, 36, 2264 (1914).

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 122.]

THE FREE ENERGY OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION AND THE ACTIVITIES OF ITS IONS.

By MING CHOW

Received November 29, 1919

CONTENTS — 1. Introduction. 2. Preparation of the Substances and Solutions. 3. Description of the Apparatus. 4. The Amalgam Electrodes. 5. Method of Procedure. 6. Measurements with the Hydrogen Mercuric-Oxide Cell. 7. Measurements with the Mercuric-Oxide Amalgam Cells. 8. The Activity Coefficients

1. Introduction.

The purpose of this research was to determine with the aid of electromotive-force measurements the free energy attending the transfer of potassium hydroxide in aqueous solution from one concentration to another, and from these free-energy decreases to derive the relative activities of the ions of the base and its activity coefficients at various concentrations. The principle of the method is substantially identical with that involved in the investigations of MacInnes and Parker¹ on potassium chloride and of Ellis², and of Noyes and Ellis³ on hydrochloric acid

With respect to the significance of the term activity, it may be recalled that this is a concept introduced by G. N. Lewis⁴ as a quantitative expression of the mass-action effect of imperfect solutes (those which exert an effect not proportional to their concentration), and shown by him to be thermodynamically related to various other properties. Thus the activity is the "effective concentration" from an equilibrium or the thermodynamic standpoint. The most general of the thermodynamic relations, one indeed which may well be regarded as the most concrete definition of activity, is that afforded by the equation

$$-\Delta F = N R T \log (a_1/a_2),$$

in which R is the perfect-gas constant, and $-\Delta F$ represents the decrease in the free energy of the system attending the transfer at the absolute temperature T of N mols of any substance (thus of an ion) from a solution of any concentration in which its activity is a_1 to another solution of any concentration in which its activity is a_2 . When dealing with ions we may substitute for their activities a_1 and a_2 , the products $\alpha_1 c_1$ and $\alpha_2 c_2$, in which α_1 and α_2 are activity coefficients (analogous to ionization coefficients) representing the factors by which the concentrations c_1 and c_2 of the substance must be multiplied to give the activities of the ions.

The most direct way of determining the free-energy decrease attending

¹ *THIS JOURNAL*, 37, 1445-1461 (1915)

² *Ibid.*, 38, 737-762 (1916).

³ *Ibid.*, 39, 2532-2544 (1917)

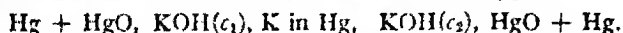
⁴ *Proc. Am. Acad.*, 43, 259-293 (1907); *Z. phys. Chem.*, 61, 129-165 (1908).

the transfer of ions from one concentration to another, and thereby of determining their relative activities, is the measurement of the electromotive force of cells in which such a transfer takes place; for the relation between these quantities is expressed by the simple equation

$$-\Delta F = E N F,$$

in which E is the electromotive force of a cell in which a given transfer of ions takes place when N faradays or NF coulombs of electricity pass through it.

The cells studied in this investigation were of the type



The potassium amalgam (K in Hg) was used in the form of a dropping electrode. The potassium hydroxide concentrations were varied from 0.003 to 0.84 N . The temperature was always 25°.

The investigation was carried out with the aid of a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington, for which I wish to express my indebtedness. To Professors D. A. MacInnes and A. A. Noyes I wish also to extend my thanks for valuable suggestions in connection with the research and for assistance in the preparation of this article for publication.

2. Preparation of the Substances and Solutions.

The mercury used was purified by blowing air through a mass of it covered with dil. nitric acid, and by distilling it in a current of air at 5-10 mm. pressure.

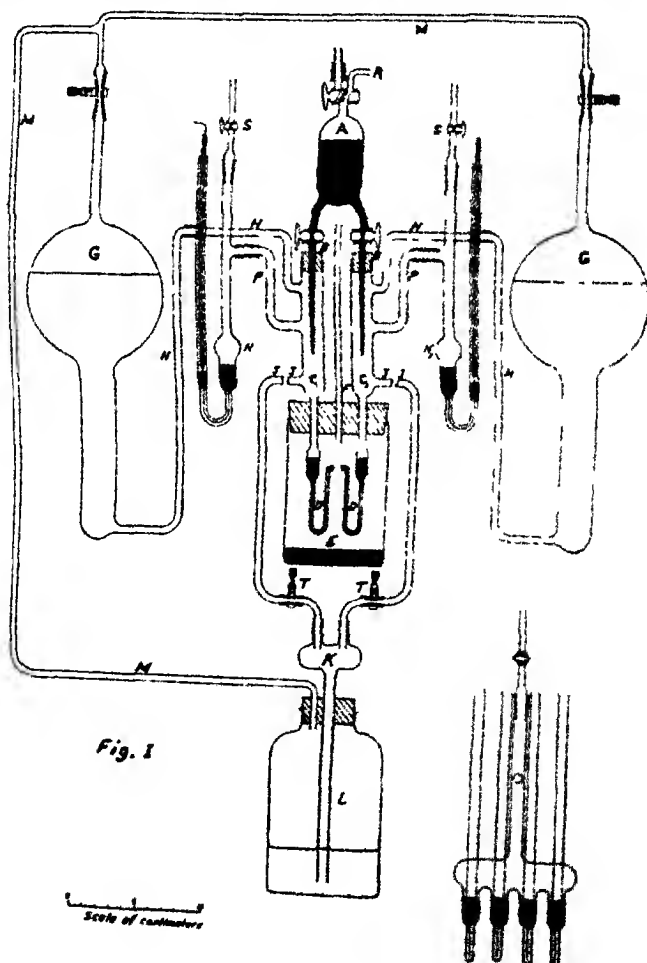
The mercuric oxide employed was a chemically pure commercial preparation.

The potassium amalgam was made by electrolyzing a pure 2 N potassium hydroxide solution (prepared as described below) between a cathode consisting of 250 cc. of mercury placed in the bottom of a 1000 cc. conical flask and an anode of platinum foil immersed in 600 cc. of the alkali solution placed above the mercury, a current of 1.5 amperes being passed for about 2 hours. The amalgam was first washed 3 times with water, and was then separated from the film of liquid and from the solid potassium hydroxide which gradually formed (through action of the moisture), by passing it through capillary tubes successively into 3 evacuated glass flasks. The amalgam was finally collected in a 500 cc. Pyrex flask, to the neck of which was sealed a glass tube carrying a stopcock (as shown in inverted position in Fig. 2 below). This method yielded a liquid amalgam containing about 0.2 atom per cent. of potassium with only a thin film of a white, solid substance. The method seems simpler than that of MacInnes and Parker, and yields equally satisfactory results.

The potassium hydroxide solution was prepared by electrolyzing with a strong current a concentrated solution of potassium hydroxide (purified

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by alcohol) over a mercury cathode till a large quantity of amalgam crystals had formed. These crystals were separated from the mercury by pouring the mass through a Büchner funnel, were washed with water and transferred to a large resistance glass bottle containing "conductivity water" closed with a stopper carrying a water-sealed exit tube. The decomposition of the amalgam became nearly complete after 3 or 4 days, the action being hastened by placing in the solution a platinum gauze connected with the amalgam by a platinum wire. The solution was then drawn through a tube containing a small asbestos filter into a nitrogen-filled Pyrex flask and the liquid was boiled under reduced pressure to expel the air. The solution was kept under nitrogen, and the flask was



fitted with tubes so that portions of it could be drawn off when needed without coming into contact with the air. The potassium hydroxide solutions so obtained were 0.5 to 0.8 *N*. They were standardized by titration with a weighed portion of constant-boiling hydrochloric acid, prepared as described by Hulett and Bonner,¹ with the help of methyl red, using a weight buret. The more dilute solutions were made by adding weighed portions of this stock solution to conductivity water in a weighed flask, boiling them under reduced pressure, and weighing the flask again to determine the exact concentration.

3. Description of the Apparatus.

The whole apparatus is shown in Fig. 1.

The vessel A is the reservoir containing the amalgam. This vessel was connected below with 3 capillary tubes, of which only 2 (lettered B) are shown in the figure. These passed through rubber stoppers into the cells C, through which the dropping amalgam fell through the overflow tubes D into the vessel E, open to the atmosphere through the tube F. These amalgam electrodes are described in detail in Section 4 below.

The 3 potassium hydroxide solutions of different concentrations were contained in 3 Pyrex glass bulbs G (of which only two are shown). From these the solutions flowed through the connecting tubes H H into cells C, and emerged from them through the outlet J into the larger tube K and the bottle L. The space above the liquid in vessels G and L was filled with nitrogen at atmospheric pressure, which was kept constant automatically because of the free communication between these vessels through the tubes M.

The 3 half-cells N₁, N₂, N₃ (of which only 2 are shown), containing the mercury, mercuric oxide, and potassium hydroxide solution previously saturated with it, were connected through tubes P with the 3 cells C containing the dropping electrodes. The half-cells were made of Pyrex glass, each having 4 separate electrode compartments at the bottom, as shown in the sketch in the lower right-hand part of the figure, which represents an elevation at right angles to that in the main drawing.

4. The Amalgam Electrodes.

The first experiments were made with a flowing amalgam electrode of the cup form used by Lewis and Kraus,¹ Lewis and Keyes,² and MacInnes and Parker;³ but it was not possible to find the conditions under which satisfactory results could be secured. A modified form of dropping electrode was therefore devised. This consisted simply of a small tube of about one mm. bore, to the lower end of which was joined a slightly tapering capillary tube about 1.5 cm. long and of such diameter that 14 g.

¹ *THIS JOURNAL*, 31, 390 (1909).

² *Ibid.*, 33, 1462 (1910).

³ *Ibid.*, 34, 120 (1912).

or one cc. of pure mercury flowed through it per minute when there was a column of mercury 19 cm. in height above the capillary. Three of these capillary tubes were made of such dimensions as to give an equal outflow of mercury. These were joined, each through a stopcock, to the bottom of a glass cylinder (A in the figure) which served as a reservoir for the amalgam.

The following table shows typical results which were obtained with dropping electrodes of this kind, and also the best results which were observed with flowing electrodes of the cup type. The cell measured was $\text{Hg} + \text{HgO}$, NaOH (0.25 *M*), $\text{Na}_2\text{O} \cdot 0.006 \text{ Hg}$, NaOH (0.04 *M*), $\text{HgO} + \text{Hg}$. The first column gives the time in minutes after the flow was started; the second column the electromotive force in millivolts shown by the capillary dropping electrode, and the third column that shown by the flowing cup electrode. The results have no absolute significance, as the concentrations were only roughly determined.

TABLE I.
Constancy of the Electromotive Force with Dropping Electrodes.

Time Min	Electromotive force	
	Dropping electrode Mv	Cup electrode Mv
1 5	93 78	83 0
3 0	93 79	88 5
4 0	93 80	90 0
5 0	.	90 8
6 0	...	91 7

5. Method of Procedure.

In making a series of measurements the amalgam was first introduced into the receiver A. This was first thoroughly cleaned and dried, care being taken that none of the stopcock grease got into the tubes. The capillary tubes were then completely filled with pure, dry mercury up to and through the stopcocks. The reservoir was connected, as shown in Fig. 2, with the inverted glass flask U containing the stock of amalgam through a tube V closed with rubber stoppers at both ends and provided with a side-arm with a stopcock. The whole arrangement was evacuated through the side-arm, and the stopcock W was opened, allowing the amalgam to flow down into the reservoir A. The flask and connecting tube were then removed and dry nitrogen was admitted to the empty space in the reservoir; a collapsible rubber bulb filled with dry nitrogen being attached to the tube R, so as to keep the pressure equal to that of the atmosphere.

The mercuric oxide half-cells were set up as shown in Fig. 1. The potassium hydroxide solutions used in them were previously boiled to expel air, and shaken for 5 to 10 hours under nitrogen in sealed Pyrex glass pipets with a little mercury and the mercuric oxide. The whole mixture was

then charged into the half-cells up to the level of the side-arms by breaking off the tips of the pipets, air being excluded by previously filling the cells with nitrogen.

The potassium hydroxide solutions were then introduced into the apparatus. The overflow tubes D were filled with mercury, serving as a seal for the 3 cells C, and these were completely filled with the 3 potassium hydroxide solutions to be investigated. The bulbs G were charged with the solutions and connected with the cells C, as were also the mercuric oxide half-cells N. The reservoir A containing the amalgam was set in place, with its capillaries dipping into the solutions, and by slight suction applied at the stopcock S the half-cells N and the connecting tubes H and P were completely filled with the solutions.

The whole apparatus (except the tube K and the bottle L) was supported on a frame within a thermostat, with the water standing at the level of the bottom of the rubber stoppers in the cell C.

In making an experiment, the solutions were started flowing through the apparatus, by opening the screw-clamps T, at a rate of about 50 cc per minute through each cell. After half a minute the amalgams were allowed to flow in through the fully opened stopcocks, at the rate of about one cc. per minute into each cell. Measurements of the electromotive force between the mercuric oxide half-cells N_1 and N_2 , and between N_2 and N_3 , were then made as rapidly as possible, the flow of the amalgam and the measurements being continued for about 4 minutes. The latest form of a Leeds and Northrup potentiometer was used for the measurements.

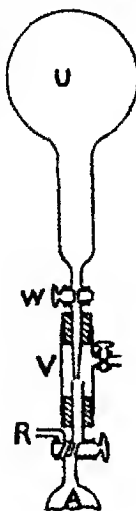


Fig. 2.

6. Measurements with the Hydrogen Mercuric-Oxide Cell.

Measurements of the electromotive force of the cells H_2 (1 atm.), NaOH (0.001 to 0.3 N), $HgO + Hg$ were made primarily to test the reproducibility of the mercuric oxide electrode, but, since the results have interest as giving the free-energy change attending the reaction



they will be presented in some detail.

The hydrogen half-cell used was the same as that described in the following article. The sodium hydroxide solution was prepared by the same method as was used for the potassium hydroxide, and the mercuric oxide half-cells were also made up just as has been already described.

The values adopted for the electromotive force were those observed after the readings had remained constant within a few hundredths of a

millivolt for an hour or more, which occurred within 2 hours after the cell was set up. These values were not changed more than a few hundredths of a millivolt by shaking the mercury half-cells, which was done in all cases. They were also corrected for instrumental errors as described by Ellis.¹ Two standard cells certified by the Bureau of Standards were used, which agreed with each other within 0.05 millivolt.

The following table contains the results. The first column shows the number of mols of sodium hydroxide per 1000 g. of water. The second column gives the mean value in millivolts of the electromotive force of the cell at 25° derived from the values observed with the 4 mercuric oxide electrodes, and reduced to a hydrogen pressure of one atmosphere (taking into account the barometric pressure and the vapor pressure of the solution). The last column of the table gives the average deviation from their mean of the 4 values observed with the separate mercuric oxide electrodes.

TABLE II.
Electromotive Force of the Hydrogen Mercuric Oxide Cell at 25°.

Mols NaOH per 1000 g. of water	Electromotive force, Mv	Average deviation Mv
0.316	926.40	0.03
0.101	926.37	0.04
0.0316	926.44	0.02
0.0103	926.08	0.05
0.00310	926.37	0.08
0.00105	926.66	0.11

It will be seen that the average deviations from the mean of the observed values for the 3 more concentrated solutions are less than 0.05 millivolt, and also that these 3 values agree with each other within nearly the same limit. This shows that the mercuric oxide electrodes, as well as the hydrogen electrode, were giving values reproducible within 0.03 to 0.05 millivolt. The somewhat greater variations in the more dilute solutions are probably due to their sensitiveness to slight concentration changes.

The average of the first 3 values is 0.92640 volt. This, multiplied by 193,000 coulombs (equivalent to 2 faradays) gives 178,800 joules as the free-energy decrease attending the reaction $\text{H}_2(1 \text{ atm.}) + \text{HgO}(s) = \text{Hg}(l) + \text{H}_2\text{O}(l)$. These values agree closely with the results of Brönsted,² which lead to the value 0.9266 for the electromotive force of the cell $\text{H}_2(1 \text{ atm.}), \text{NaOH}(0.672 M), \text{HgO} + \text{Hg}$ at 25°.

7. Measurements with the Mercuric-Oxide Amalgam Cells.

Three sets of measurements were made. In each set observations were made of the electromotive force of the combinations of mercuric oxide half-cell N, through the amalgam electrodes in C₁ and C₂ with mercuric

¹ THIS JOURNAL, 38, 749 (1916).

² Z. phys. Chem., 65, 86 (1909).

oxide half-cell N_2 , and of the combination of the half-cell N_2 through the amalgam electrodes in C_2 and C_3 with the half-cell N_2 . Just before the amalgam and the potassium hydroxide solutions were started flowing, the 4 electrodes in each of the mercuric oxide half-cells were compared with each other. The average deviation of the 4 electrodes from the mean commonly amounted to 0.05 millivolt. That one which had the electromotive force nearest to the mean was alone used for the measurements of the combination cells.

Immediately after the flow of the amalgam was started the electromotive force was unsteady but within half a minute it had become constant and remained so within a few hundredths of a millivolt for about 3 minutes. When the amalgam had mostly dropped into the solution, the values usually increased by 0.2 to 0.3 millivolt. The values of the electromotive force adopted were those observed soon after they became constant.

Table III contains the observed electromotive forces E in volts for the 3 sets of measurements, and the corresponding free-energy decreases ($-\Delta F$) in joules attending the transfer of 1 KOH from the solution whose concentration c_1 is given in the first column to the solution whose concentration c_2 is given in the second column. In the last column are given the activity coefficient ratios α_1, α_2 calculated by the equation

$$-\Delta F = RT \log (c_1 \alpha_1 / c_2 \alpha_2)^2,$$

in which the quantities α really represent the geometrical means $(\alpha_K \alpha_{OH})^{1/2}$ of the activity coefficients of the two ion constituents

TABLE III.
Electromotive Force of the Mercuric Oxide-Amalgam Cells.

Mols KOH per 1000 g. water		Electromotive force E	$-\Delta F = 96,500 E$	α_1/α_2
c_1	c_2			
0.8394	0.09396	0.10807	10439	0.917
0.09396	0.01054	0.10636	10264	0.889
0.4506	0.04407	0.11134	10744	0.854
0.04407	0.004474	0.11310*	10914	0.917
0.2895	0.02978	0.10772	10395	0.837
0.02978	0.003473	0.10730	10355	0.941

* This value was obtained by introducing hydrogen electrodes in place of the mercuric-oxide electrodes.

8. The Activity Coefficients.

In order to show the degree of concordance of the 3 sets of measurements and to combine them into a single series, the activity coefficients were plotted as ordinates against the square roots of the concentrations as abscissas. To obtain absolute values of the activity coefficients it is assumed that the value at the lowest concentration, 0.0035 molal, is 0.980, which is the value derived for the conductance ratio of potassium

hydroxide at 18° from the conductivity data of Kohlrausch¹ and the ion conductances at zero concentration of Johnston.² This value, 0.980, is intermediate between those adopted in the previous articles from this laboratory for the activity coefficient of potassium chloride³ (0.979 at 0.001 molal) and for that of hydrochloric acid⁴ (0.985 at 0.0034 molal). The method of plotting was to locate first the point $\alpha = 0.979$, $c = 0.00347$, and then the points corresponding to the last 2 activity ratios in Table III, and to draw a curve through them; then to locate on this curve the point for $c = 0.00447$, and to locate without reference to the curve the other 2 points corresponding to the 2 activity ratios given in the middle rows of the table, and to draw the best representative curve through the 5 independent points and, finally, to bring into the plot, by proceeding in the same way, the first 2 activity ratios given in the table. A second graph was plotted independently by another person in an exactly similar way except that the logarithms of the concentration (instead of its square-roots) were plotted as abscissas.

The activity coefficients read off from the 2 plots at certain round concentrations, and the means of the 2 values at each concentration, are given in Table IV. It should be noted that these activity coefficients α are really the geometrical means $(\alpha_K \alpha_{OH})^{1/2}$ of the activity coefficients of the two ion constituents, and that they represent the activity coefficients of either ion constituent only under the assumption that the two are equal. In the last 2 columns of the table are given the values of the conductance-viscosity ratio ($\Lambda\eta/\Lambda_0\eta_0$) and of the conductance ratio (Λ/Λ_0) calculated from the conductance values of Kohlrausch¹ at 18°, the Λ_0 value (237) for 18° derived by Johnston,⁵ and the viscosity data of Kamitz⁶ at 25°.

TABLE IV.
The Activity Coefficients of Potassium Hydroxide

Mols per 1000 g. of water	Activity coefficients			Conductance viscosity ratio	Conductance ratio
	I	II	Mean		
1.00	0.800	0.786	0.793	0.877	0.776
0.70	0.772	0.772	0.772	0.880	0.804
0.50	0.764	0.766	0.765	0.884	0.831
0.30	0.770	0.768	0.769	0.889	0.855
0.20	0.795	0.791	0.793	0.891	0.870
0.10	0.845	0.847	0.846	0.910	0.900
0.03	0.921	0.919	0.920	0.939	0.936
0.01	0.960	0.961	0.961	0.963	0.962
0.003	0.983	0.981	0.982	0.980	0.980

¹ "Landolt u. Börnstein, Tabellen," 1912, p. 1104.

² THIS JOURNAL, 31, 1015 (1909).

³ See Ellis, *ibid.*, 38, 760 (1916).

⁴ Noyes and Ellis, *ibid.*, 39, 2543 (1917).

⁵ THIS JOURNAL, 31, 1015 (1909).

⁶ Z. phys. Chem., 22, 340 (1897).

It will be seen from these results, as was found by Ellis in the case of hydrochloric acid, that:

(1) The activity coefficient at first decreases with increasing concentration, but passes through a minimum at a concentration of about 0.5 molal, and then increases rapidly.

(2) Up to concentrations of 0.5 molal the activity coefficient has a much smaller value than the conductance-viscosity ratio (thus 7% smaller at 0.1 molal, and 11% smaller at 0.2 molal), thus again showing that this ratio, even at these moderate concentrations, is not even an approximate measure of the effective ionization of largely ionized substances.

CAMBRIDGE, MASS

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 123.]

THE ACTIVITIES OF THE IONS IN SOLUTIONS OF MIXED ELECTROLYTES.

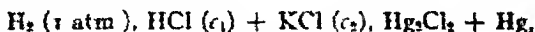
BY MING CHOW

Received November 29, 1919

CONTENTS.—1. Introduction. 2. Apparatus and Experimental Procedure. 3. Preparation of the Substances and Solutions. 4. The Experimental Results. 5. Discussion of the Activity Coefficients

1. Introduction.

This investigation consisted in measurements of the electromotive force of voltaic cells of the type



in which the separate concentrations c_1 and c_2 were varied, but their sum $c_1 + c_2$ was kept constant, namely, in these experiments, at 0.1 *N*. The purpose of the research was to determine directly the value of the product of the activities of the hydrogen ion and chloride ion, and to draw conclusions as to the separate activities of these two ions in the mixture.¹

A similar research with the same object in view has already been published by Loomis, Essex, and Meacham;² but as it was found possible in the present investigation to secure more constant and reproducible electromotive forces, and as the data lead to conclusions somewhat different from those drawn by these authors, it seems desirable to present here the results of my measurements. Reference should also be made to the work of Harned,³ who measured the same type of cell, but kept the concentration of the hydrochloric acid, not that of the mixed electrolytes, constant.

This research was carried out at the suggestion of Prof. A. A. Noyes.

¹ In regard to the concept of activity and activity coefficients here employed, see the first section of the preceding article.

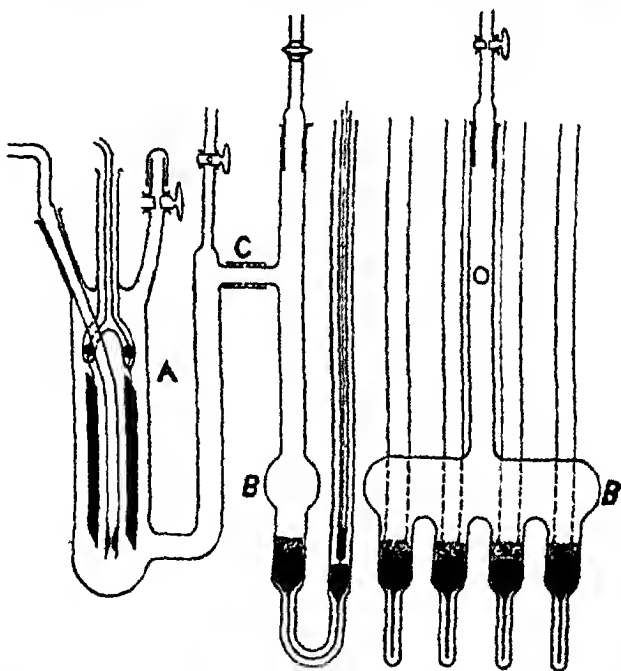
² This JOURNAL, 39, 1133 (1917).

³ *Ibid.*, 38, 1983 (1916).

with the aid of a grant made to him by the Carnegie Institution of Washington. I wish to express my indebtedness to him also for his assistance in the preparation of this article for publication. I wish also to thank Dr. Duncan A. MacInnes for his interest and suggestions throughout the progress of the work

2. Apparatus and Experimental Procedure.

The form of calomel half-cell used is shown in the figure, in which 2 cross-sections of the half-cell at right angles to each other are represented. It will be seen that these half-cells had 4 compartments containing 4 separate calomel electrodes. The hydrogen half-cell used differs from



that described by Noyes and Ellis¹ only in the respect that the inlet tube for the hydrogen was set in a separate tubulus with a ground joint, so that it could be removed for cleaning.

Before introducing the solutions into the calomel half-cell, they were saturated with calomel by agitating the mixture of mercury, calomel, and the solution in a sealed pipet at room temperature in a shaking machine for 5 to 10 hours. In most cases the air was boiled out under reduced pressure, and the solutions were transferred to the half-cell without coming into contact with the air. This precaution of removing the

¹ THIS JOURNAL, 30, 2324 (1912)

air seemed, however, to make little, if any, difference; but the agitation of the calomel with the solution is essential.

The method of making the observations and the corrections applied were the same as those described by Ellis.¹ Two standard cells were employed which had been recently certified by the National Bureau of Standards.

3. Preparation of the Substances and Solutions.

The mercury was purified by blowing air through a mass of the liquid covered with dil. nitric acid, and subsequently distilling it in a current of air at reduced pressure.

The calomel was made electrolytically as described by Ellis.

The hydrogen was made by the electrolysis of sodium hydroxide solution. It was purified by passing it through a wash bottle containing water kept slightly acid with hydrochloric acid with the aid of an indicator. For use in the cells a 0.1 *N* hydrochloric acid solution was made by diluting by weight with freshly distilled conductivity water the constant boiling acid, prepared as described by Hulett and Bonner.² The accuracy of its acid content as given by Hulett has been repeatedly checked in this laboratory by gravimetric determinations of the chlorine as silver chloride.

The potassium chloride used was an imported preparation, which had been dried for several days at 100°. A solution of this containing 0.1 mol. of potassium chloride per 1000 g. of water was made up. To determine how nearly neutral this solution was, its hydrogen concentration was determined by placing in it a hydrogen electrode and combining it with a calomel half-cell containing potassium chloride at the same concentration. The various solutions prepared were thus found to have hydrogen ion concentrations lying between 1 and 5×10^{-7} . The larger of these quantities would produce an error of only 0.5% in the acid concentration in the most dilute solution investigated (0.0001 molal). Fused potassium chloride, on the other hand, gave a solution distinctly alkaline, with an hydroxide ion concentration of about 10^{-6} .

The mixtures of hydrochloric acid and potassium chloride were prepared by weighing out definite quantities of the two 0.1 molal solutions. This yielded mixtures always containing just 0.1 mol of chloride per 1000 g. of water. The contents in hydrochloric acid and potassium chloride were calculated from the weights taken.

4. The Experimental Results.

Table I contains the results of the experiments. The first and second columns give the concentrations, in millimols per 1000 g. of water, of the hydrochloric acid and potassium chloride, respectively. The third col-

¹ THIS JOURNAL, 38, 748-749 (1916).

² THIS JOURNAL, 38, 748-749 (1916).

column contains the corresponding values of the electromotive forces of the cells at 25°. These values are the means of the observations for the 4 calomel electrodes with the 2 hydrogen electrodes (which always checked each other within about 0.01 millivolt). The fourth column contains the average deviations of these values from the mean. The fifth column gives the reduced barometric pressure. The sixth column gives the observed values reduced to a hydrogen pressure of one atmosphere. These values were corrected in the usual way, taking into account the vapor pressure of the solutions and variation of the barometric pressure from one atmosphere, as described in detail by Ellis

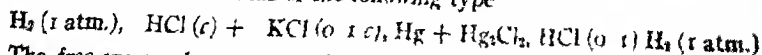
TABLE I
Electromotive Force of the Cells at 25° in Millivolts

Millimols per 1000 g. water		Electromotive force observed	Average deviation	Barometric pressure	Electromotive force corrected
HCl	KCl				
100.0	0.00				399.04*
31.71	68.29	428.35	0.04	76.04	428.70
10.00	90.00	458.07	0.06	76.04	458.52
3.065	96.93	488.55	0.05	76.04	488.90
1.055	98.94	515.52	0.01	76.01	515.89
1.000	99.00	516.98	0.03	76.82	517.21
0.339	99.66	544.68	0.08	76.02	545.06
0.316	99.68	546.50	0.03	75.65	546.96
0.304	99.70	547.72	0.08	76.22	548.06
0.223	99.78	555.45	0.11	76.02	555.83
0.100	99.90	574.48	0.08	76.02	576.43

* This value is that found by Ellis (*loc. cit.*, p. 754). It agrees substantially with the values (0.3990, 0.3991, 0.3988) found by others as summarized by Lewis, Brighton and Sebastian (*THIS JOURNAL*, 39, 2757 (1917)). In their summary, these authors made a slight mistake in quoting Ellis' value as 0.3988 instead of 0.3990.

5. Discussion of the Activity Coefficients.

By subtracting the first of the electromotive-force values given in the last column of Table I from the succeeding values there is obtained the electromotive force of cells of the following type



The free-energy decreases obtained by multiplying these differences by 96500 are those attending the transfer of 1 HCl from the 0.1 molal hydrogen chloride solution to the mixture in which the hydrogen chloride concentration is c . From these free energies we may calculate the ratio of the product of the activity coefficients (a_{H} and a_{Cl}) of the hydrogen ion and chloride ion constituents in the mixture to the same product in the 0.1 molal solution. Namely, when one faraday (F coulombs) of electricity passes through the cell from left to right, there is a transfer of one mol of hydrogen ion from a solution in which its activity (or effective concentration) is 0.1 ($a_{\text{H}})_{0.1}$ to one in which its activity is ca_{H} , and a transfer of one mol of chloride ion c .

is 0.1 (α_{Cl})_{0.1} to one in which its activity is 0.1 (α_{Cl}); whence follows the following expression for the free-energy decrease ($-\Delta F$):

$$-\Delta F = (E - E_{0.1})F = RT \log \frac{0.1 (\alpha_H)_{0.1} (\alpha_{Cl})_{0.1}}{c \alpha_H \alpha_{Cl}}$$

The following table gives the so-calculated ratios of the products of the activity coefficients:

TABLE II
Activity Coefficients of Hydrochloric Acid in the Mixture.

Millimols HCl per 1000 g of water	$\frac{\alpha_H \alpha_{Cl}}{(\alpha_H)_{0.1} (\alpha_{Cl})_{0.1}}$
100.00	1.000
31.71	0.994
10.00	0.987
3.065	0.988
1.055	1.003
1.000	1.005
0.339	1.003
0.316	1.005
0.304	0.995
0.223	1.003
0.100	1.003

These data show that the activity coefficient of the hydrochloric acid has substantially (within 1%) the same value in all the mixtures. Thus the deviations from unity show no steady progression, and the maximum deviation of 1.3% corresponds to a variation in the electromotive force of 0.65 millivolt. In other words the product of the activities of the ions is proportional to the product of the concentrations of hydrogen ion and chloride ion constituents, even when the concentration of the acid is varied from 0.0001 to 0.1 *N* provided, as in this case the total concentration of electrolyte in the solution remains constant.

If we make the assumption rendered probable by the considerations recently presented by MacInnes,¹ that the chloride ion has the same activity in solutions in which the chloride concentration is the same, whatever may be the cation associated with it, we reach the conclusion that the hydrogen ion has an activity proportional to its concentration. In other words, that it behaves as a perfect solute, so long as the total ion concentration in the solution remains unchanged. Since the hydrogen ion might be expected to be especially sensitive to disturbing influences, this result substantiates the principle that the activity coefficient a/c of the uni-valent ions of largely ionized substances is in general a function of the total salt or total ion concentration, and not of its own concentration.

If, on the other hand, we do not make the assumption that the chloride ion has the same activity in the different mixtures, we must accept the

alternative that it has a variable activity which is just compensated by an opposite variation in the activity coefficient of the hydrogen ion. As this alternative is improbable, the result lends support to the assumption itself, namely, to the principle that the activity of the chloride ion in solutions of different largely ionized univalent chlorides or of mixtures of them is determined by its own concentrations and is independent of the cations associated with it.

Finally, reference must be made to the results of Loomis, Essex and Meacham,¹ who measured the electromotive force of the same type of cells also with potassium chloride and hydrochloric acid at a total concentration of 0.1 *N*. Their data, unlike those above presented, show with increase in the proportion of potassium chloride, a progressively increasing deviation of the observed electromotive forces from those calculated under the assumption that the activity coefficient of the hydrochloric acid remains constant. Moreover, the variation is in the direction that corresponds to greater activity of the chloride ion in the acid than in the salt solution, which accords with the results of Noyes² on the relative effects of hydrochloric acid and the alkali element chlorides on the solubility of thalious and plumbous chlorides. The deviation amounts, however, to only 1.28 millivolts even in the mixture most dilute in hydrochloric acid (that 0.01 *N* in hydrochloric acid and 0.09 *N* in potassium chloride); while the check measurements with the same mixtures often differed by 0.5 millivolt.³ This deviation of 1.28 millivolt, if not due to experimental error, corresponds to a variation of 5% in the product of the activity coefficients. Inasmuch as the calomel electrode used by these investigators showed accidental variations 10 times as great as those used in the research here presented, it seems justifiable to give greater weight to the data of this article and to regard as most probable the conclusion drawn from them as to the constancy of the activity coefficients in the mixture.

CAMBRIDGE, MASS

¹ THIS JOURNAL, 39, 1133 (1917).

² *Z. phys. Chem.*, 9, 609, 623 (1892).

³ It may be mentioned that the authors referred their concentrations to one liter of solution, while in the present research they are referred to 1000 g. of water; but calculation shows that this affects the ratio of the concentrations in the two limiting cases by only 0.1%.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I. 5]

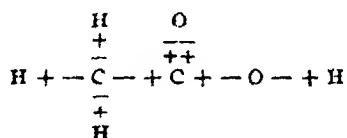
THE ELECTRONIC CONSTITUTION OF NORMAL CARBON CHAIN COMPOUNDS, SATURATED AND UNSATURATED.

BY EUSTACE J. CUY (COUYUMBOPOULOS)

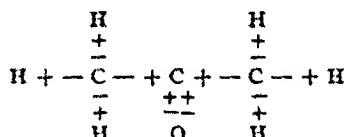
Received December 2, 1919

In a recent paper on "The Electronic Constitution of Acetoacetic and Citric Acids and Some of Their Derivatives," Hanke and Koessler,¹ making the implicit assumption that organic compounds are polar in nature, give the following formulas based on the reactions of these compounds:

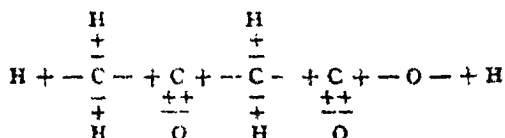
Acetic acid:



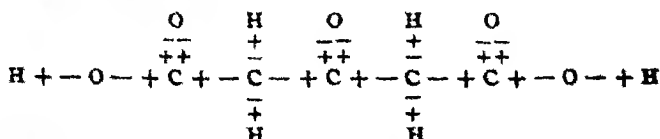
Acetone:



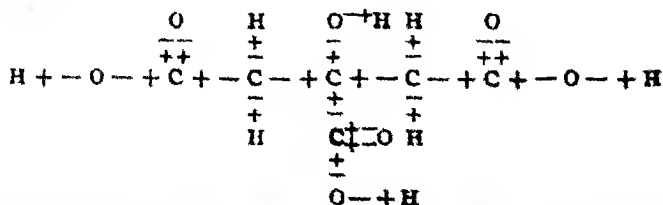
Acetoacetic acid



Acetone dicarbonic acid



Citric acid:



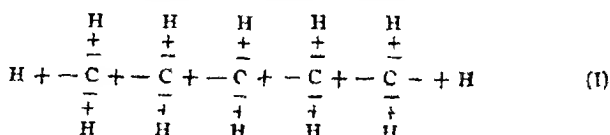
A striking fact is to be observed, namely, that in all 5 of the above

given carbon chains the carbon atoms are alternately positive and negative.

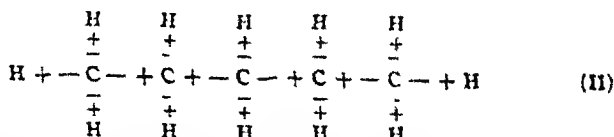
The present paper will adduce evidence tending to establish the fact that in a chain of carbon atoms the tendency is for these atoms to appear alternately positive and negative whenever possible, and that the alternating sign of the charge in the above cited 5 examples is not accidental.

We shall exclude from consideration in the present paper carbon chains including aryl groups, since there is no generally accepted notion of the structure of the benzene ring

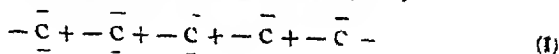
If it be conceded that organic compounds are polar in nature, as are inorganic compounds,¹ although possibly to a less degree, then the structure of a member of the methane series will be either



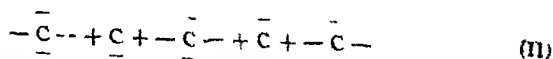
or



or, omitting the hydrogen atoms for the sake of simplicity

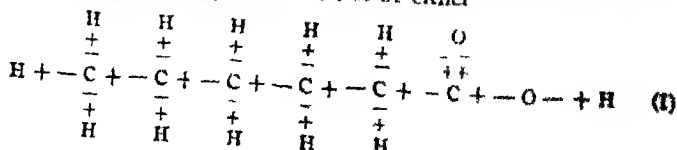


or



That is, either the positive and the negative charges will in so far as possible be evenly distributed among the carbon atoms, or the positive charges will tend to accumulate on alternate carbon atoms and the negative charges on the remaining carbon atoms

These two possibilities are not limited to the homologues of methane, but extend to the homologues of any series as, for example, that of the monocarboxylic acids. Capronic acid will be either



or

(3) differs from (5) by the same $+\bar{C} + -\bar{C}-$ group. Similarly, (2) differs from (4), and (4) from (6) by $-\bar{C}- + \bar{C}+$. But (1) differs from (2) by a $+\bar{C}-$ group, and (2) from (3) by $\left[+\bar{C} + -\bar{C}-\right] - \left[+\bar{C}-\right]$. Similar formulas may readily be written and compared in the case of other homologous series with the same result, i. e., that the members containing an even number of carbon atoms and those containing an odd number give 2 distinct series.

If Formulas II are correct, then a given property X should vary continuously for each of the 2 series the even and the odd, but should not be the same for the 2. Thus, when represented graphically, the compounds with an even number of carbon atoms should give points lying on a simple continuous curve, while compounds containing an odd number of carbon atoms should give points lying on another simple, and perhaps similar curve, not identical with the first. The addition of a single carbon atom would then cause a displacement from one curve to the other, while the addition of 2 carbon atoms should cause a displacement along the same curve. In certain instances the differences between the 2 curves may be small. In that case it is sometimes possible to show the distinctive nature of the odd and the even series by means of plots of the differences $\Delta X/\Delta n$, or even differences of higher order.

It has long been known that the melting points of monocarboxylic

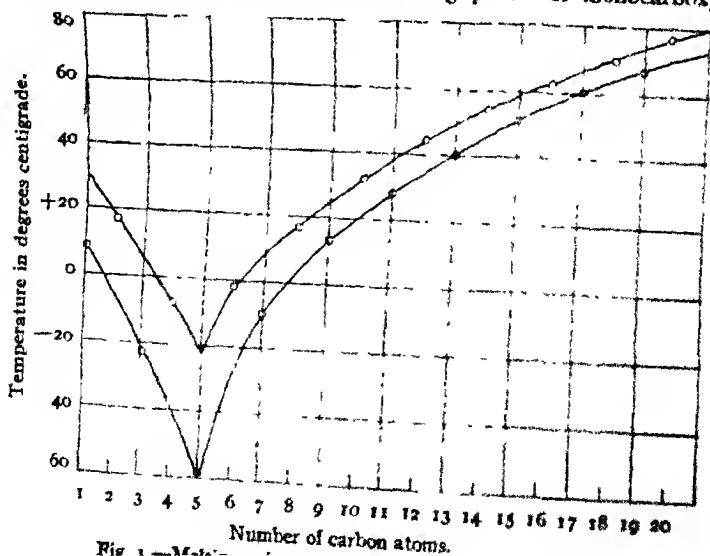


Fig. 1. Melting points.

acids¹ are alternately high and low and tend toward a common value as the number of carbon atoms increases. In Fig. 1, the melting points of the monocarboxylic acids in degrees centigrade are plotted against the number of carbon atoms in the compounds. As is to be expected on the basis of the present theory, 2 distinct simple curves are obtained which are very similar and which exhibit a break at the fifth carbon atom. This break might perhaps be accounted for on the basis of Baeyer's Strain theory (*Spannungstheorie*).²

Similar alternately high and low values of the melting points giving 2 separate and distinct curves have also been observed in the case of dicarboxylic acids.³ In Fig. 2, the melting points of the dicarboxylic acids

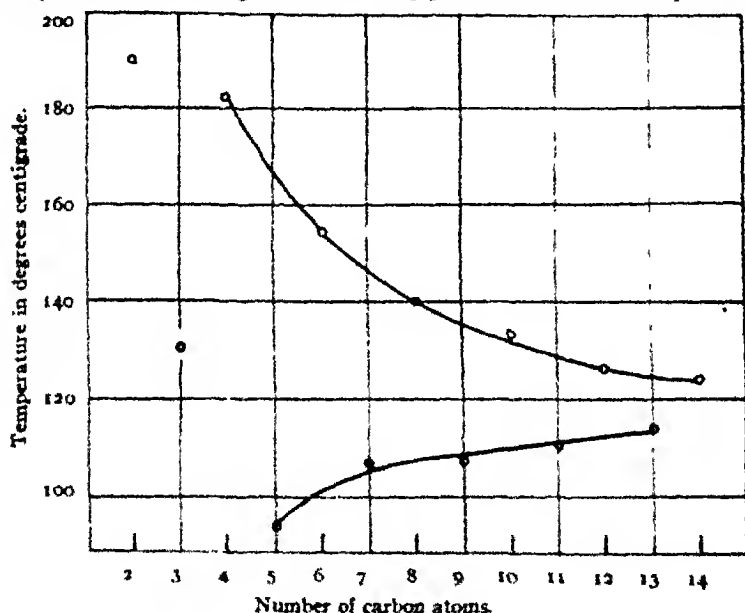


Fig. 2.—Melting points of dicarboxylic acids

in degrees centigrade are plotted against the number of carbon atoms in the compounds.⁴ Again we obtain 2 separate curves as we should expect,⁵ and again a break occurs in each curve at about the same point

¹ Baeyer, *Ber.*, 10, 1286 (1877).

² Baeyer, *ibid.*, 12, 2277 (1885).

³ Henry, *Compt. rend.*, 60, 943 (1885); Baeyer, *Ber.*, 10, 1286 (1877); Nordlinger, *ibid.*, 23, 2359 (1890).

⁴ The data for Figs. 1 and 2 were taken from "Lehrbuch der Organischen Chemie," by V. Meyer and P. Jacobson.

⁵ Falk and Nelson (*THIS JOURNAL*, 32, 1640 (1910)) offered a somewhat similar explanation for the alternately high and low values of the melting points.

as in the monocarboxylic acid series, which break might be similarly accounted for.

In Fig. 3, the melting points¹ of the normal paraffines in degrees centigrade are plotted against the number of carbon atoms. Again we obtain 2 separate curves. To make the characteristics of the curves more evi-

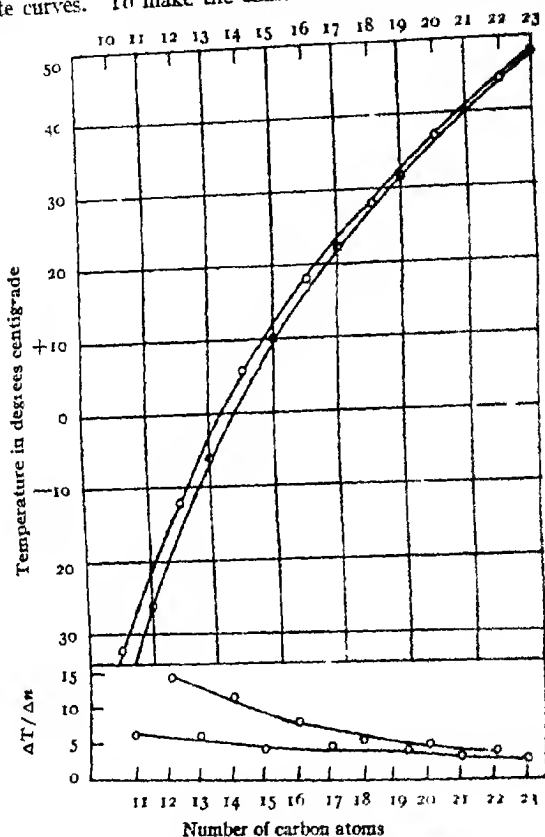


Fig. 3—Melting points of normal paraffines

dent the differences $\Delta T/\Delta n$ are also plotted against the number of carbon atoms. Similar curves result in the case of several other series. The necessary data appear in the literature. It is to be noted that the even series give a higher melting point curve than the odd series.

Biach² in his article in "*Über Regelmässigkeiten in homologen Reihen*," several years ago, gave a very large number of examples of such homologous

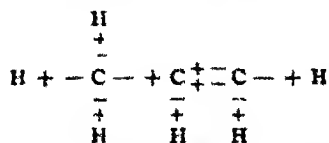
¹ The data for Fig. 3 were taken from "The Relation between Chemical Constitution and Some Physical Properties," by S. Smiles

² Biach, *Z physik Chem.*, 50, 43 (1905).

series whose melting point (or whose melting-point differences $\Delta X/\Delta n$) are alternately high and low; including paraffines, alkyl iodides and cyanides, alkylmethyl ketones, fatty acids, dicarboxylic acids, acetamides, acid anhydrides, α -oxy-fatty acids, ketonic acids, normal diamines, lactams, δ -valerolactams, dicarbonic acid anhydrides, alkyl malonic acids, and alkyl succinic acids. Also boiling points of 22 series, densities and molecular volumes of more than 20 series, viscosities of 8 series, solubilities of 3 series and several other series of constants.

Particularly in the case of the melting points, the tendency for the even and the odd carbon atoms to lie upon 2 distinct curves is very noticeable, and, while in the case of the other properties the series do not appear to be so distinct, they, nevertheless, show a like character. Although the 2 curves are not as distinct in some cases as in others, the cases where the 2 curves distinctly appear are altogether too numerous to be attributed to chance. Moreover, it is not improbable that inaccurate data may tend to mask the characteristics of the curves. The physical properties of homologous series seem therefore to support the hypothesis that alternate carbon atoms in a carbon chain tend to become positive and the rest negative.

Further evidence in support of the present hypothesis, namely, that carbon atoms in a normal carbon chain compound are alternately electropositive and electronegative, is found in the addition of hydrogen halides to unsaturated carbon compounds. Markownikoff's rule states: "When unsymmetrically constructed hydrocarbons of the series C_nH_m combine with hydrogen iodide, the iodine is added to the least hydrogenated carbon atom."¹ The rule also holds for other halogen acids. This rule follows from the present hypothesis, since the most hydrogenated carbon atom will be electronegative, the adjacent carbon atom will be electropositive and will unite with the negative radical (Cl^- , Br^- , I^-); that is, each carbon atom tends to assume either an entirely electropositive or electronegative character whenever possible. According to our hypothesis the electronic formula of propylene is



for in accordance with this hypothesis we find the reaction

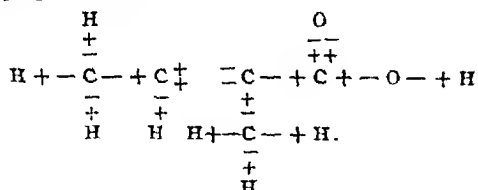


Similarly,



¹ Saytzeff, *Ann.*, 179, 396 (1873)

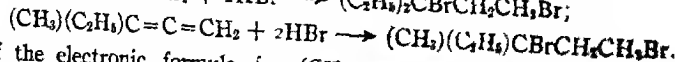
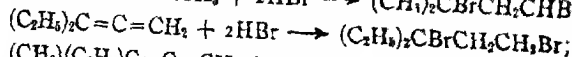
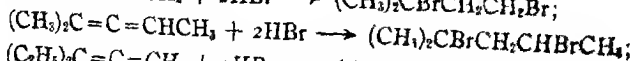
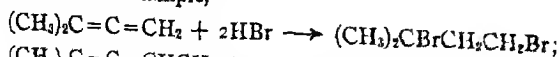
It has been shown, however, that Markownikoff's rule fails in several cases. For example, when hydrogen iodide is added to α -ethylidene-propionic acid, $[\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{COOH}]$, the compound $\text{CH}_3\text{CH}_2\text{Cl}(\text{CH}_3)\text{COOH}$ should be obtained according to Markownikoff's rule, while, instead, the compound $\text{CH}_3\text{CHICH}(\text{CH}_3)\text{COOH}$ is obtained.¹ This case, which proves the insufficiency of Markownikoff's rule, is very readily accounted for by the present hypothesis. The electronic formula for α -ethylidene-propionic acid is



The first and fourth carbon atoms are, respectively, entirely electronegative and electropositive, and the third and second almost entirely so; and the atoms are arranged in the order C negative, C positive, C negative, C positive. When hydrogen iodide is added to this compound, it is to be expected that the electronegative radical I^- will go to the second carbon atom which is electropositive, and the electropositive H^+ atom to the third carbon atom which is electronegative. This has been found to be the case.

The present hypothesis, therefore, embraces Markownikoff's rule since it accounts for all the cases where this rule holds. That it is more general follows from the fact that it also accounts for those cases in which Markownikoff's rule fails.

The addition of hydrogen bromide to unsaturated hydrocarbons having 2 adjacent double bonds offers further evidence corroborating the present theory. According to Ipatieff's rule: "Dihydrobromides are produced by the addition of hydrogen bromide to hydrocarbons of the allene series, in which both bromine atoms are not attached to neighboring carbon atoms."² For example,³



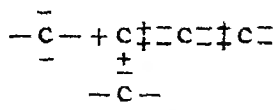
If the electronic formula for $(\text{CH}_3)_2\text{C}=\text{C}=\text{CH}_2$ were, for example, $(\text{CH}_3)_2\text{C}^+\text{---}\text{C}^+\text{---}\text{C}^+\text{---}\text{H}$, or some other similar one, where the positive

¹ Cohen, "Organic Chemistry for Advanced Students," 2nd Edition, II, p. 256.

² Ipatieff, *Chem. Centr.*, 70, II, 17 (1899).

³ Ipatieff, *ibid.*, 67, I, 835 (1896); 70, II, 17 (1899).

and negative charges were evenly distributed among the carbon atoms, the addition product ought to be $(\text{CH}_3)_2\text{CBrCHBrCH}_3$ or $(\text{CH}_3)_2\text{CHCHBrCH}_2\text{Br}$. According to the present hypothesis the carbon atoms will tend to become alternately entirely positive and negative, as far as possible. Omitting the hydrogen atoms, the electronic formula of $(\text{CH}_3)_2\text{C} = \text{C} = \text{CH}_3$ is therefore:

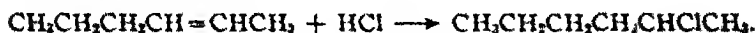
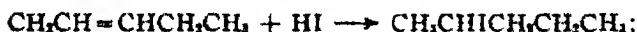
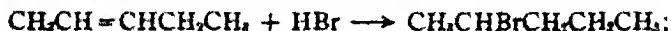


This accounts for the fact that bromine does not add on adjacent carbon atoms, since adjacent carbon atoms are not of the same electronic character. The present hypothesis, therefore, accounts for Ipatieff's rule also.

A very interesting question which Markownikoff's rule does not answer is: How will HX (when X is Cl , Br or I) add when both atoms of an unsaturated hydrocarbon at the double bond are equally hydrogenated, as for example, in $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$. Saytzeff, who first asked this question, answered it only for the particular case of $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$, showing experimentally that¹



In a straight chain unsaturated hydrocarbon containing an odd number of carbon atoms, it would be expected that the negative radical should add on the second, fourth or an even carbon atom. Since carbon atoms tend to become alternately positive and negative and since the first and last carbon atoms have 3 hydrogen atoms adjoined, they and all the odd carbon atoms will consequently be electronegative and the even ones will be electropositive. Very few cases have been investigated, but they all agree with the present theory. We have²



On the other hand, an unsaturated carbon chain with an even number of carbon atoms may give one or both of the possible addition compounds depending on the nature of the reaction products.

* Another example of a similar type is³

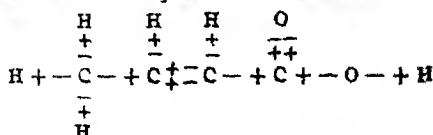


¹ Saytzeff, *Ann.*, 179, 297 (1875).

² Beilstein, "Handbuch der Organischen Chemie," 3rd Edition, I, pp. 176, 193, 134.

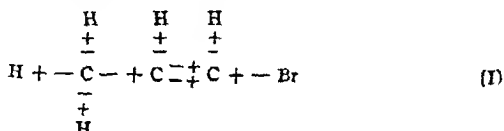
³ Meyer and Jacobson, *loc. cit.*, p. 935.

This reaction also is in harmony with our view since in

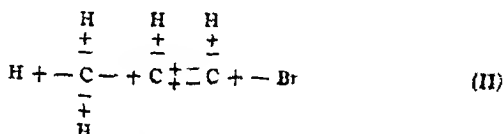


the second carbon atom is electropositive and should add on the electro-negative iodine.

Another case¹ for which there is no rule giving any information as to the course of addition of a hydrogen halide is that of $\text{CH}_3\text{CH}=\text{CHBr}$. It has been found that both possible products are formed, namely, $\text{CH}_3\text{CH}_2\text{CHBr}_2$ and $\text{CH}_3\text{CHBrCH}_2\text{Br}$. The electronic formula for $\text{CH}_3\text{CH}=\text{CHBr}$ may be either

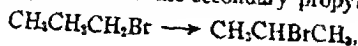


or

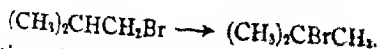


Since both formulas come equally near to fulfilling the condition for alternately positive and negative carbon atoms, both electronic isomers will coexist and consequently both reaction products should be obtained. This has been found to be the case.

Finally, the isomeric rearrangement of alkyl halides can be readily accounted for, on the basis of the present hypothesis. It is a well-known fact that primary propyl bromide in the presence of catalyzers such as aluminum bromide, goes over to the secondary propyl bromide,² thus:



and similarly,³



The reverse reactions, however, do not take place. On the other hand, primary butyl bromide does not rearrange to give the secondary bromide.⁴ An explanation of the striking differences in the behavior of these compounds appears not to have been suggested heretofore. The present hypothesis accounts for the fact that the first 2 reactions take place only

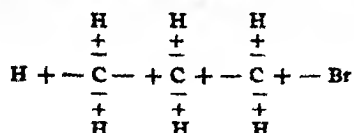
¹ Cohen, *loc cit* p 115

² Aronstein, *Ber.*, 14, 1, 607 (1881), *ibid.*, 16, 391 (1873)

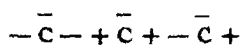
³ Eltekoff, *ibid.*, 8, 1244 (1873).

⁴ V. Meyer and Muller, *J. prakt. Chem.*, 46, 182 (1892)

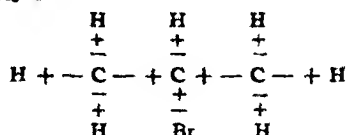
as written above as well as for the non-occurrence of a similar reaction in the third case. The electronic formula for $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ is



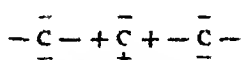
i. e.,



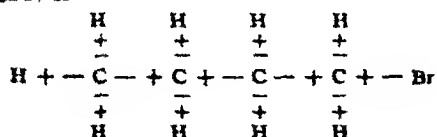
and for $\text{CH}_3\text{CHBrCH}_3$ is



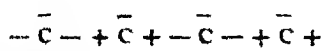
i. e.,



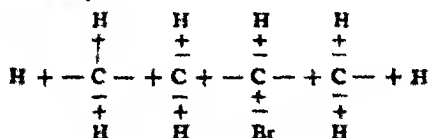
It is evident that of the 2, the second formula comes the nearer to fulfilling the condition for alternately positive and negative carbon atoms. Consequently the primary bromide under proper conditions will rearrange to give the secondary bromide, while the reverse reaction will not take place. The reactions of $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$ can be readily accounted for on the same basis. The electronic formula of primary butyl bromide $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br})$ is



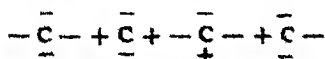
i. e.,



and that of the secondary is



i. e.,



It is evident that the carbon atoms in the first formula are approximately alternately positive and negative, while in the second formula the charges are more evenly distributed. According to our hypothesis, of 2 possible isomers that one is more stable which has its carbon atoms alternately

positive and negative, as far as possible. Consequently the transformation of the primary to the secondary bromide should not occur, which is in accordance with the facts. There are no observations available relating to the reverse reaction in this case.

It is to be kept in mind that the present theory is founded on 2 assumptions. First, that carbon compounds are of the same nature as inorganic compounds; that is, they are polar. For example, as NaCl is assumed to be $\text{Na}^+ \text{Cl}^-$, so CH_4 is assumed to be $\overset{+}{\text{H}} \overset{+}{\text{H}} \overset{+}{\text{C}} \overset{+}{\text{H}} \overset{+}{\text{H}}$. Second, that the carbon atoms in a chain compound tend to become alternately positive and negative, and the more nearly this condition is fulfilled, the more stable is the compound. The first assumption may in a certain sense be considered self-evident, since the division of chemical compounds into organic and inorganic is universally admitted to be arbitrary and since the difference between the two classes seems to be one of degree and not of kind.¹ Many writers on organic chemistry in recent years have employed electronic formulas for organic compounds.²

With the aid of these two assumptions it thus becomes possible to account for a great many facts which otherwise appear unrelated on the basis of the common theory of the structure of carbon chain compounds. The fact that the various phenomena discussed above may be accounted for on the basis of the assumptions made, serves as a support for the correctness of these assumptions.

Summary.

Assuming that carbon compounds are polar in nature and that carbon atoms in a chain tend to assume alternately positive and negative charges, it has been shown that the fluctuation in the various physical properties of these compounds such as melting points, boiling points, and so forth, between the even and the odd members of a given series may be accounted for. Various reactions, in which these compounds take part, such as the addition of halogen acids and the isomeric rearrangement of the halides may likewise be accounted for, on the basis of these assumptions.

WORCESTER, MASS

¹ Harkins and King (THIS JOURNAL, 41, 976 (1919)) state. "Thus even carbon compounds seem to be distinctly polar, because they have greater affinity for electrons than hydrogen, etc., and a smaller affinity than chlorine, etc. The polarity is, of course, very much less than that of salts."

² Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914), Fry, *ibid.*, 39, 34 (1908); 36, 248 (1914); 34, 664 (1912); Fry, Z. physik. Chem., 76, 385, 398 (1911); 80, 29 (1912); 82, 665 (1913); Nelson, Beans and Falk, THIS JOURNAL, 35, 1810 (1913); Falk and Nelson, *ibid.*, 32, 1637 (1910); 33, 1140 (1911), L. W. Jones, *ibid.*, 36, 1268 (1914); L. W. Jones and Werner, *ibid.*, 40, 1257 (1918); Hanke and Koessler, *ibid.*, 40, 1726 (1918).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

OBSERVATIONS ON THE RARE EARTHS. X. THE PURIFICATION AND ATOMIC WEIGHT OF SAMARIUM.¹

By A. W. OWENS, C. W. BALKE AND H. C. KREMERs.

Received December 26, 1919.

Introduction.

This investigation was undertaken as a part of a general program mapped out in 1911 for work on the purification and atomic weights of the different rare earth elements. The samarium material was purified to a high degree preliminary to the determination of its atomic weight. The ratios oxide to chloride, and oxide to chloride hydrate, were found to be unsatisfactory and were replaced by the ratio chloride to silver.

Purification of Reagents.

The water used was redistilled from alkaline permanganate and gave no test for chlorides in the nephelometer. The oxalic acid was prepared by twice recrystallizing c. p. acid from water acidified with nitric acid and once from water alone. The acid thus prepared gave no residue on igniting a 20 g. sample. c. p. nitric and hydrochloric acids were redistilled from a quartz flask as needed. Hydrogen chloride was prepared by dropping c. p. sulfuric acid into c. p. hydrochloric acid and drying the gas by passing it through beads moistened with sulfuric acid. Nitrogen was prepared by burning ammonia and air in a quartz tube containing copper gauze and was then purified by removing the water, carbon dioxide, arsine, etc. The air was purified in the same manner. The apparatus for the purification of hydrogen chloride, nitrogen and air has been previously described.² The silver used was very kindly donated by Dr. H. C. Kremers. Its preparation has been previously described by him.³

Preparation of Pure Samarium Oxide and Chloride.

(a) *Separation of Samarium from Lanthanum, Praseodymium and Neodymium.*—The source of the material used in obtaining the pure samarium material was some 400 pounds of cerium-earth double sulfates from the Welsbach Mantle Co. These sulfates contained all of the members of the cerium group, but as the original source of the material was monazite sand there was very little europium or gadolinium present. Most of the cerium had been removed for commercial purposes and the yttrium earths had been roughly removed by precipitating out the cerium earths as double sulfates with a saturated solution of sodium sulfate.

¹ Part of a thesis submitted by A. W. Owens to the Graduate School of the University of Illinois as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Kremers, H. C., *This Journal*, 40, 398 (1918).

³ *Lac. cit.*

The double sulfates were boiled with a strong solution of sodium hydroxide until they were completely decomposed. The solution was diluted and the hydroxides were washed with boiling water until they were free from sulfates. In order to remove the remaining cerium, the hydroxides were dissolved in nitric acid, the solution was made nearly neutral, heated to boiling and potassium bromate added. As the red fumes of bromine appeared, marble dust was added to keep the solution nearly neutral and the solution was boiled until some of the filtered liquid failed to give a test for cerium with hydrogen peroxide. The small amount of cerium basic nitrate and the excess marble were filtered off. The rare earth oxalates from this solution were ignited to oxides and these were dissolved in dil. nitric acid. In order to convert these nitrates into the magnesium earth double nitrates for fractionation, as first recommended by Demarcay,¹ a quantity of nitric acid equal to the amount used in the solution of the oxides was neutralized with magnesium oxide, and the two solutions filtered and united. This solution was then fractionally crystallized for the separation of the samarium material. When the most soluble fractions, containing the bulk of the samarium, began to crystallize poorly, they were diluted, filtered, and the earths precipitated as oxalates in order to remove any impurities of the common elements which might be present.

When no more samarium appeared at the soluble end the fractionation was discontinued. The samarium oxalate was ignited, and the oxide was again converted into the magnesium samarium double nitrate as described above. In the second series of fractionations the most soluble fractions were set aside when no more absorption lines of neodymium were visible through 10 cm. of a saturated solution.

(b) Separation of Samarium from Europium and Gadolinium.—The material from the previous fractionation now contained some europium and gadolinium and possibly a very small amount of yttrium earths. After the yttrium earth nitrates had been removed, by running the samarium magnesium double nitrates through about 180 fractionations with 30% nitric acid, bismuth magnesium double nitrate was added at the soluble end. According to Urbain and Lacombe,² the bismuth magnesium double nitrate crystallizes between samarium and europium with gadolinium still more soluble than europium. After about 40 crystallizations of this series the first 6 determinations were made. Before making any further determinations it was thought advisable to fractionate the bismuth and samarium double nitrates still more, even though for some time the material had shown no other adsorption lines than those of samarium. The material was put through about 150 more crystalliza-

¹ *Compt. rend.*, 130, 1019 (1900)

² *Ibid.*, 137, 793 (1903).

tions before the final series of oxide-chloride determinations were made. The samarium chloride-silver determinations were made with the very best material.

(c) **Conversion into Oxide.**—The samarium material used for the atomic weight determinations was taken from the middle series of the samarium bismuth magnesium nitrates described above. The nitrates were thoroughly fused in a porcelain dish and the oxides and basic nitrates thus formed were dissolved in as little hydrochloric acid as possible. After evaporating this solution to a syrupy condition, it was poured into a large volume of distilled water. The bismuth oxychloride was allowed to settle and the supernatant liquid siphoned off. The cold solution containing the samarium chloride and magnesium chloride was saturated with hydrogen sulfide in a 10-liter flask, and was then digested on the steam bath until the brown coloration entirely disappeared and the bismuth sulfide settled out. The bismuth sulfide was filtered off and the solution again saturated with hydrogen sulfide. This was repeated until no further precipitation of bismuth sulfide was obtained. The hydrogen sulfide was removed by forcing filtered air through the boiling solution. The solution was made 1% acid with nitric acid and samarium oxalate precipitated out with hot dil. oxalic acid.

In precipitating samarium oxalate it was found best to do so from a boiling 1% nitric acid solution, using a boiling solution of dil. oxalic acid as the precipitant. By adding the oxalic acid until the precipitate first formed, just failed to redissolve and then cooling the solution rapidly it was found possible to obtain a very fine precipitate which was crystalline, settled rapidly, and washed well on a Büchner funnel. These oxalates were dried and ignited in platinum dishes in an electric oven in order to convert them into oxides. The oxides were then dissolved in nitric acid and the samarium precipitated as hydroxide by passing ammonia vapors into the flask while the solution was being agitated. The hydroxides were washed by decantation until they started to become colloidal and were then washed on a Büchner funnel. The oxalate and hydroxide precipitations were carried out alternately, 3 times for each sample. The oxalates were ignited at 800° for 6 hours and then at 900° for 2 hours. In this way it was hoped that all the carbonate first formed would be decomposed to the oxide.

(d) **Conversion into Anhydrous Chloride.**—The method of converting samarium oxide into anhydrous chloride was somewhat similar to that used by Baxter in preparing other rare earth chlorides. Instead of the bottling apparatus used by the latter, a quartz reaction flask, first described by Egan,¹ was used to obtain the transformation. This had the advantage that the oxide was changed to chloride in the apparatus in

¹ THIS JOURNAL, 35, 363 (1913).

which it was weighed and the chloride was also weighed in the same apparatus.

The samarium oxide, ignited as described above, was transferred to the previously weighed reaction flask while still hot, and the outlet and inlet tubes were inserted and their air-tight caps were adjusted. The reaction flask was then placed in a desiccator and the latter placed in the balance room for one hour. After loosening one of the caps to equalize the pressure, the flask was hung in the balance case and weighed at intervals of $\frac{1}{2}$ hour until it had come to equilibrium.

All weighings were made on a very sensitive Ruprecht balance used exclusively for atomic weight work, in a special cork-lined room, the temperature of which seldom varied more than 3° . All weighings were made by substitution, using a similar flask as tare. The weights were either of platinum or of gold-plated brass and were calibrated to 0.01 mg. All weights were corrected to vacuum before being used in any calculation. The specific gravity of the brass weights was taken as 8.4, of the platinum weights as 21.5, of the samarium oxide as 8.247,¹ of samarium chloride as 4.465,² of samarium chloride hydrate as 2.383,³ and of silver as 10.53. The atomic weights were taken as follows: oxygen, 16.0; chlorine, 35.46; silver, 107.88; and hydrogen, 1.008.

The oxide in the flask was moistened with water and then dissolved in pure hydrochloric acid. The oxide always dissolved to a clear amber-colored solution without any apparent effervescence or spattering. The reaction flask was then attached to the drying train by means of the two ground joints and enclosed in an electrically heated oven having glass sides through which the progress of the dehydration could be watched. This oven also protected the flask from the fumes of the laboratory during the time it was connected to the train. The oven was heated to 130° , and a brisk stream of air was passed through the flask thus driving off most of the excess water. The temperature was then dropped to 105° , and hydrogen chloride, passed in to cause the formation of samarium chloride hydrate, as this procedure allowed the excess solution to creep up the sides of the flask, and exposed a larger surface for dehydration. The first 5 molecules of water were removed below 105° , by a current of air and hydrogen chloride, in from 10 to 12 hours. This point was shown by the absence of moisture in the cooler portions of the exit tube. The proportion of hydrogen chloride was now increased and the temperature was gradually raised to 190° where the last molecule of water was expelled. Hydrogen chloride alone was now passed through the flask and the temperature gradually raised to 360° , where it was held for one hour. The over

¹ *Chem. News*, 51, 145 (1885).

² *Compt. rend.*, 140, 1339 (1905).

³ *ibid.*, 140, 1339 (1905).

was then removed, the stream of hydrogen chloride was stopped, and the samarium chloride was fused either with a Bunsen flame or with an electric pot furnace. There was no evidence that the samarium chloride was appreciably volatile at its melting point. According to Matignon,¹ anhydrous samarium chloride melts at 686°. When free from oxychloride the samarium chloride melts to a reddish liquid which does not wet the bottom of the quartz flask. If, however, any oxychloride is present the melt wets the flask, attacks it, and fuses with much more difficulty. After the samarium chloride was fused the flask was cooled in an atmosphere of hydrogen chloride and then air was passed through the flask until all traces of hydrogen chloride were removed. By first adjusting the cap on the outlet tube, and then the one on the inlet tube, the flask could be sealed without admitting any undried air. The samarium chloride was weighed in a manner similar to that described for the oxide.

At first nitrogen was used in the early part of the dehydration, but this was found to be unnecessary. Furthermore, it was found that samarium chloride heated for some time in a current of nitrogen lost chlorine, and was reduced to samarous chloride (SaCl_2). According to Baxter, nitrogen prepared in this way contains some hydrogen and these experiments seem to confirm his statement for tests showed that hydrogen chloride was given off and not chlorine. The samarous chloride was a purplish brown crystalline mass and had the other properties ascribed to it by Matignon.² The use of nitrogen was discontinued, because of the danger of reducing the samaric chloride.

All the samples of samarium chloride dissolved completely in cold water. In order to test the hydrogen ion concentration of the samarium chloride solution, samples from a preliminary run were treated with the following indicators. rosolic acid gave yellowish pink; methyl orange gave yellow; congo red gave orange; phenolphthalein gave a colorless solution; and litmus gave red-violet. These results, according to Washburn, indicate a hydrogen ion concentration of about 10^{-8} .

The Ratio of Samarium Oxide to Samarium Chloride.

In about 1911 Prof. C. W. Balke and his associates began a series of atomic weight determinations on various elements of the rare earth family. As a few preliminary experiments showed that the oxide-sulfate and hydrated sulfate ratios were unreliable they decided to use the oxide-chloride ratio. Egan,³ Sears,⁴ Engle,⁴ Hopkins,⁵ Kremers,⁶ and Wichers,⁶ have used this ratio for atomic weight determinations

¹ *Compt. rend.*, 141, 1230 (1905).

² *Loc. cit.*

³ *THIS JOURNAL*, 36, 833 (1915).

⁴ *Ibid.*, 39, 33 (1917).

⁵ *Ibid.*, 38, 2332 (1916).

⁶ *THIS JOURNAL*, 40, 1666 (1918).

The first 6 determinations were made in 1913 with material from the middle of the best series. Although this material showed no other absorption spectra than that of samarium, one year was spent in making further fractionations from nitric acid of 1.30 sp. gr. As the results from the next 8 determinations were in no better agreement than those from the first 6, it was decided to obtain the oxide from different sources. Dr. Kremers found that the oxide chloride ratio gave consistently higher results than the chloride silver ratio in the determination of the atomic weight of dysprosium. Dr. Wichers found that it was impossible to prepare pure erbium oxide by the ignition of the oxalate. Samarium nitrate and samarium hydroxide were, therefore, used as the source of oxide in the next 8 determinations. These samples were ignited at 900° and then ground in an agate mortar, the process being repeated 3 times in order to obtain as pure an oxide as possible. These results were no better than the previous ones so this ratio was abandoned because of the difficulty of obtaining pure samarium oxide. The average atomic weight for the 22 determinations by this ratio was 153.0

The Ratio Samarium Chloride Hexahydrate to Samarium Chloride.

Samarium chloride hexahydrate was prepared from the purest oxide and was recrystallized 5 times from a water solution. It was hoped that a dependable ratio might be obtained between samarium chloride hexahydrate and samarium chloride, but due to the difficulty of obtaining a hydrate of constant composition this ratio was found to be useless. The hexahydrate when exposed to dry air at 27° will lose water continuously and finally fall to a powder.

The Ratio Samarium Chloride to Silver.

The ratio of a rare earth chloride to silver was first used by Baxter and Chapin¹ to determine the atomic weight of neodymium and was later used by Baxter and Stewart² to determine the atomic weight of praseodymium. Stewart and James³ also used this ratio in their revision of the atomic weight of samarium.⁴ Egan tried to use this ratio in his determination of the atomic weights of yttrium, but for some unknown reason he failed to get concordant results. The ratio was not used again in this laboratory until it was successfully carried out by Kremers in his determination of the atomic weight of dysprosium.

In order to become familiar with the manipulations necessary in this ratio, a few determinations of pure fused sodium chloride against silver

¹ THIS JOURNAL, 33, 1 (1911)

² *Ibid.*, 37, 516 (1915)

³ *Ibid.*, 39, 2605 (1917)

⁴ At the time Stewart and James published their article entitled, "A Revision of the Atomic Weight of Samarium," the laboratory work on the present investiga-

were made. The results were quite comparable to those of Richards and Wells for the same ratio.

The anhydrous samarium chloride was weighed in the reaction flask, in which it had been dehydrated, and was dissolved in conductivity water. The solution was quantitatively transferred to a 1.5 liter glass-stoppered Jena Erlenmeyer flask, and diluted to 400 cc. Assuming the atomic weight of samarium to be 151.0, within a few tenths of a milligram of the calculated weight of silver was weighed out, and dissolved in dil. redistilled nitric acid in a liter Jena Erlenmeyer flask fitted with a column of bulbs, 50 cm. high, to retain any spray. The silver nitrate solution was diluted to 400 cc. and added gradually to the dilute samarium chloride solution while the latter was being violently agitated. After agitating for 3 hours in a motor-driven shaking machine, the solution was allowed to stand for 12 hours, and the clear supernatant liquid was then tested in a nephelometer for an excess of either chlorine or silver. All work which involved materials affected by light was done in a dark room. After testing the supernatant liquid, portions of standard silver nitrate or sodium chloride solutions were added from weighing pipets until exact equivalence was reached. The amount of silver used, as silver nitrate, was added to the amount originally weighed out, and the silver equivalent of the sodium chloride added was subtracted from the total silver. It was necessary to add sodium chloride when too much silver had been weighed out, or when too much silver nitrate had been added. After each addi-

THE RATIO OF SAMARIUM CHLORIDE TO SILVER.

No.	Fraction	SmCl ₃	Ag weighed out	Ag added	Ag total	$\frac{\text{SmCl}_3}{\text{Ag}}$	Atomic weight.
1	42	6.47502	8.14202	+0.01608	8.15810	0.793692	150.49
2	42	4.03877	5.09024	—0.00941	5.08083	0.794903	150.90 (SmOCl)
3	43	4.23293	5.36673	—0.00745	5.35928	0.793567	150.43
4	43	4.34537	5.47543	+0.00120	5.47663	0.793442	150.41
5	44	3.84046	4.74751	+0.09251	4.84002	0.793480	150.42
6	45	3.32317	4.31449	—0.12629	4.18820	0.793460	150.42
7	32	2.96369	3.73081	+0.00423	3.73504	0.793480	150.42
8	33	3.34818	4.21583	+0.00353	4.21936	0.793527	150.44
9	34	3.27999	4.13128	+0.00205	4.13333	0.793546	150.44
10	35	3.00394	3.78617	+0.00152	3.78769	0.793396	150.40
11	36	2.36481	2.97873	+0.00097	2.97970	0.793640	150.47
12	37	3.68616	4.64535	+0.00042	4.64577	0.793444	150.41
13	38	3.17435	4.00033	—0.00013	4.00020	0.793548	150.44
14	39	2.81639	3.54905	+0.00027	3.54932	0.793501	150.43
15	40	3.13553	3.95087	+0.00068	3.95155	0.793500	150.43
16	41	2.91019	3.66900	—0.00154	3.66744	0.793520	150.44
17	42	4.15775	5.23920	+0.00055	5.23973	0.793504	150.43
18	43	3.32503	4.18985	—0.00033	4.18952	0.793650	150.47
19	44	2.06632	2.62794	+0.00156	2.62950	0.793430	150.41

tion the flask was shaken for 2 hours and was then allowed to stand from 8 to 12 hours before testing again.

The samarium chloride for determinations 1-4 was obtained from the last 4 determinations of the oxide-chloride ratio. In determinations 5-13 the anhydrous chloride was obtained by introducing a saturated solution of samarium chloride into the flask and dehydrating as described above. In determinations 14-19 the anhydrous chloride was obtained from the determinations of the ratio hydrated chloride to anhydrous chloride. Although the material for these last 6 determinations was purified more than the previous material, the atomic weights are virtually the same.

The results of this ratio are shown in the table on page 521.

Summary.

1. Samarium material was obtained from rare earth residues purchased from the Welsbach Mantle Co. The cerium was removed by means of bromine and marble. Lanthanum, praseodymium and neodymium were removed by fractionation of the rare earth magnesium double nitrates, first from a water solution and then from nitric acid of 1.30 sp. gr. Europium and gadolinium were removed by fractionation of the rare earth magnesium double nitrates along with bismuth magnesium double nitrate. The final purification was the alternate precipitation of samarium material as hydroxide and oxalate and 5 recrystallizations of this material as hydrated chloride.

2. The oxide-chloride ratio was found unsatisfactory due to the difficulty of obtaining pure oxide. Oxide was obtained by igniting the oxalate, nitrate and hydroxide, but the results were equally discordant.

3. The hydrated chloride-anhydrous chloride ratio was found unsatisfactory due to the difficulty of obtaining pure samarium chloride hexahydrate.

4. The anhydrous chloride-silver ratio was altogether satisfactory and these values are to be taken in preference to all others.

5. The results of this investigation confirm the results of Stewart and James as to the value of the atomic weight of samarium.

[CONTRIBUTION FROM THE COLOR LABORATORY OF THE U. S. BUREAU OF CHEMISTRY.]

SOME ASPECTS OF THE BEHAVIOR OF CHARCOAL WITH RESPECT TO CHLORINE.¹

BY G. S. BOHART AND E. Q. ADAMS.

Received January 8, 1920.

I. Object of Investigation.

Preliminary work on the absorption of chlorine by charcoal revealed considerable variations in the capacity of a single sample of charcoal, for which no cause was apparent except variations in the humidity of the chlorine-laden gas. It therefore seemed worth while to make a careful study of the effect obtained with a number of different kinds of charcoal by varying the humidity while controlling the temperature of the charcoal tube. The results of this work were so interesting that the effect of variations of temperature, of velocity of gases through the charcoal, of charcoal thickness and of gas pressure on the surface of the charcoal were also studied.

II. Description of Apparatus.

1. For the Removal of Chlorine from Air (Dynamic Method).—This consisted essentially of a charcoal reaction-chamber I, Fig. 1, suspended in a water thermostat. Chlorine from the cylinder X and air entering at A were mixed in the tower J, after which they passed through a layer of charcoal in I. Gases not absorbed were drawn by the suction V through an absorption train, either T₁ or T₂. In order that the apparatus for the thermostat could be handled conveniently, it was suspended from a shelf so constructed that it served as a cover to the bath. The latter consisted of a square copper box resting on a vertically sliding shelf attached by means of overhead pulleys to counter weights. When it was necessary to replace the charcoal charge or manipulate the apparatus, ordinarily in the water, it was necessary only to lower the bath (see dotted line), after which the various parts were easily accessible. To secure uniform and effective circulation, as well as more constant temperature, a wooden compartment O was constructed within and fastened to the copper bath. The perforated lid of the inner box was attached to the cover of the outer copper bath.

In the diagrammatic cut of the heating system, S₁ is a switch for starting the motor and stirrer P; L₁ is a lamp resistance to regulate the speed of the motor; S₂ is a switch to the heating system; L₂ is a lamp resistance to conduct the right current for the safe manipulation of the relay R; T is the mercury *thermoscope*; H is the "make and break" on the relay

¹ The writers wish to express their appreciation of the hearty cooperation and helpful criticism given them in the course of the work by Lieut. Col. A. B. Lamb

and L_h shows the heating lamps which in practice consist of $1' \times 12'$ show case lights located in the 4 corners of the outer thermostat bath.

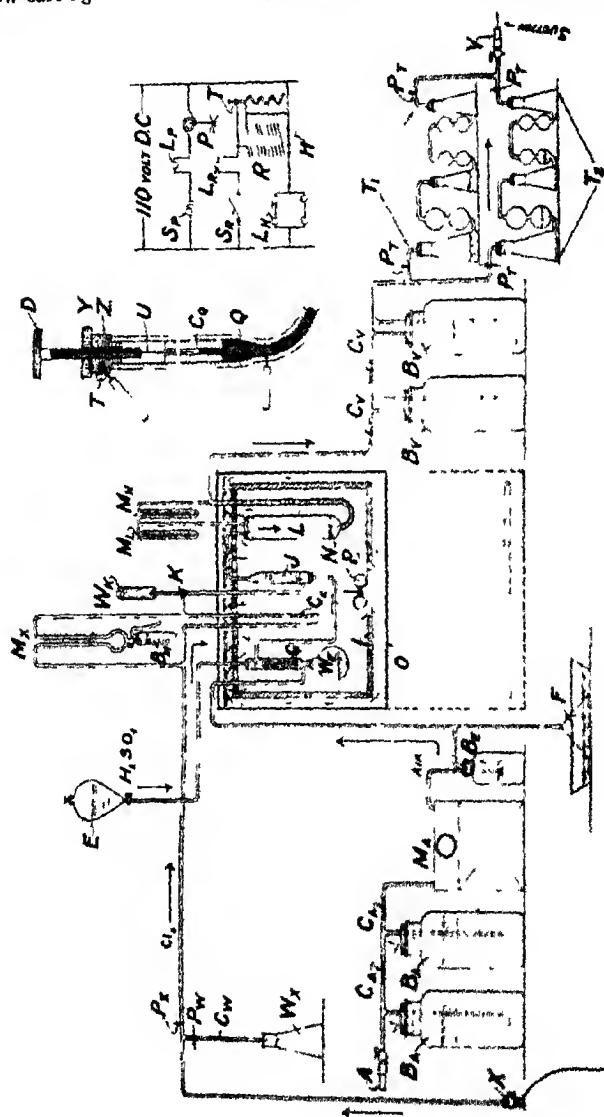


FIG. 1

serves as a bearing for the thumbscrew D, and as a cover for the spiral glass tube filled with mercury, Q. T is one of the electrical connections.

The quantity of chlorine from the reservoir was measured with a flow-meter M_x so constructed that the capillary C_x was located in the thermostat. Pentachloro-ethane¹ for the manometer was stored in a reservoir B_m , from which, when needed, it was forced into the graduated tube by opening the stopcock and blowing in the open side tube.

After a rough adjustment of the chlorine flow had been made at X the necessary refinement required to keep the flow meter manometer within 0.2 mm. of the correct reading, was made by the use of pinch-cocks P_w and P_x . The capillary tube C_x was so chosen that the manometer reading was always in the neighborhood of 10 cm. To correct for the density change of pentachloro-ethane with temperature, 0.08% per degree was either added or subtracted as conditions required. Daily replacement of the manometer liquid prevented the solution in it of any considerable amount of chlorine.²

While the flow of chlorine was being adjusted at the beginning of an experiment, that gas was diverted to the soda-lime tube W_4 by the 2-way stopcock K. During the experiment proper, chlorine flowed through K into the chamber J where with the assistance of glass wool it was mixed with air which entered at the bottom of the same device.

Air under pressure was supplied at the valve A. By allowing an excess of air to bubble at all times from the tubes in the pressure regulating bottles, B_a , variations in the line air pressure were prevented from reaching the gas meter M_a . The air velocity was determined by the depth of the tubes below the water surface in the pressure regulators B_a . To control the moisture content of the air, two separate saturators were employed, each containing sulfuric acid of the strength necessary to produce the desired humidity. By bubbling the air through the first of these, B_s , a moisture content approximating that desired was obtained. To complete the saturation, the air next passed up through the tower G (located in the thermostat) which was filled with glass beads over which flowed more of the same acid. This latter was furnished from the reservoir E and collected in the flask W_5 .

To prevent vibrations attending the bubbling of air through B_s from interfering with the readings of the manometers M_a , M_i and M_m , a broad funnel F inverted in a pan of water furnished an effective cushion.³

¹ This compound was prepared from trichloro-ethylene by passing chlorine through the boiling liquid in the presence of iron filings.

² Failure to do this occasionally resulted in the formation of chlorine gas bubbles when the laboratory temperature rose suddenly.

³ This arrangement gives a cushioning effect out of all proportion to the size of the device, in this case equivalent to that of an air reservoir of about 0.54 cu. meter capacity; with a sufficiently large pan, equivalent to that of a closed air cylinder with

The air-chlorine mixture from J entered the top of the reaction chamber 4 , where it encountered the charcoal resting on a perforated porcelain plate.

To measure the pressure on the upper surface of the charcoal and the drop in pressure experienced by the gas while passing through the absorbent, manometers M_1 and M_2 were employed.

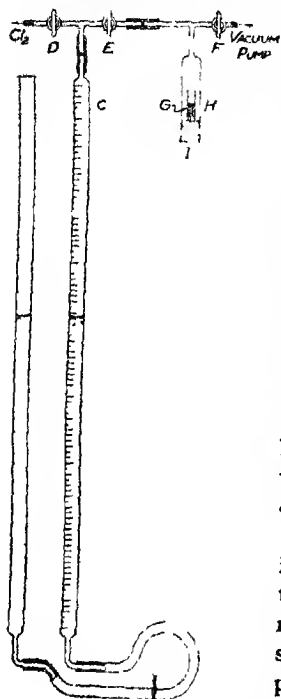


Fig. 2.

The lower manometer connection extended through the exit tube of the charcoal chamber clear into the space N below the charcoal.

Suction was controlled by the valve V and kept constant by the pressure regulating bottle B_1 ; the action of these is *mutatis mutandis*, the same as that of bottles B_2 .

Samples for analysis were obtained in the absorption trains T_1 and T_2 .

2. For the Absorption of Air-Free Chlorine.—Chlorine from a reservoir, Fig. 2, was introduced through D and collected over salt brine in C. At the end of an hour the rate of contraction of chlorine through solution and reaction became sufficiently slow to be neglected.

A weighed amount of charcoal was placed in the weighing bottle G which was then transferred to the chamber H closed by the rubber stopper I. Without opening E, the space above G was connected to a vacuum pump through F, until the pressure was constant,¹ after which F was closed. The time was noted when E was opened to allow chlorine to enter H and volume readings were taken at frequent intervals thereafter.

III. Analytical Procedure.

To determine, in the dynamic method, the time at which chlorine first appeared beyond the charcoal, the escaping gas stream was led through one of the absorption trains, filled with a potassium iodide solution containing starch, Fig. 1. After the blue color had appeared, quantitative results were obtained by diverting the gas mixture to the other absorption train, containing potassium iodide solution without starch, for definite lengths of time. The point at which hydrochloric acid (resulting from the cata-

¹ Usually about 2 mm.

lytic action of the charcoal) first appeared, was determined by backward graphical extrapolation of the acid titer.¹

In samples containing both iodine and hydrochloric acid, the iodine was titrated first with sodium thiosulfate, using starch; the hydrochloric acid was then titrated with sodium hydroxide, using "brom-cresol purple" as indicator.² To prevent carbon dioxide from interfering with the end point, as soon as a fugitive pink color indicated that the titration was nearly finished, air freed from carbon dioxide by soda lime was bubbled through the solution for 2 minutes, after which the neutralization was completed.

It will be noted that no attempt has been made to distinguish between chlorine and any other substance capable of liberating iodine from potassium iodide solution.

IV. Preparation and Properties of Charcoals Used.

With the exception of A the 6 charcoals employed in this work were prepared for use in gas masks and were made from coconut shells. Lot A, for the sake of comparison, was made from ordinary wood and was not manufactured with the object of absorption in view.

V. Analysis of the Typical Chlorine-Charcoal Transmission Curve.

Fig. 3 is drawn to bring out the various factors which influence the shape of the typical charcoal-chlorine transmission curve.

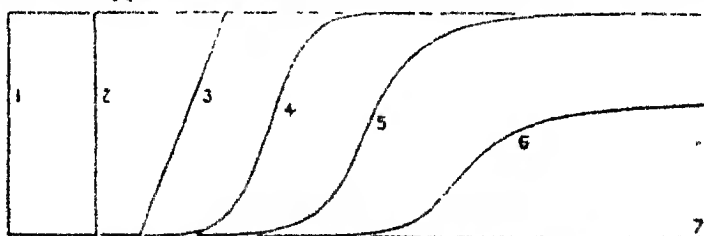


Fig. 3.—Different possible types of transmission curves.

1. Line 1 represents the limit approached by the chlorine-transmission curve as the effectiveness of the absorbing³ material diminishes. Chlorine appears beyond the charcoal in full concentration at once.

2. An ideal⁴ charcoal, infinitely fine-grained and reacting instantaneously

¹ In several of the later experiments the same method was used for the chlorine.

² "Brom-cresol purple" is dibromo-*o*-cresol-sulphonphthalein. Lubs and Clark, *J. Wash. Acad. Sci.*, 6, 482 (1916); *J. Bacteriol.*, 2, 1-34, 109-136, 191-236 (1917). For the method cf. Lewis, Adams and Lanman, *THIS JOURNAL*, 37, 2656 (1915).

³ Since it has not been found possible in this work to distinguish between absorption and adsorption, or even chemical action, the word "absorption" will be used throughout this paper, unless otherwise indicated, as a general term comprising all three.

⁴ Any capacity for chlorine which remains unused at the time when toxic amounts of chlorine are being transmitted is wasted, so far as concerns practical use of the charcoal. In the ideal case this residual capacity will, therefore, be reduced to a minimum.

with chlorine, would give a curve of Type 2. The length of the lower horizontal portion represents the absorption capacity of the charcoal.

3. Such a charcoal in a rectangular container, with the thickness varying uniformly from one side to the other, would give a transmission curve of Type 3.

4. The cases just considered have assumed that the absorption reaction is instantaneous. If this assumption be not made, it becomes necessary to make some assumption for the rate of reaction, and the simplest probable one is that the rate of the reaction is proportional to the fraction of its capacity which the charcoal still retains, and to the concentration of chlorine in the gas. This amounts to assuming that the reaction is monomolecular with respect to chlorine (which is probably true) and that the charcoal is perfectly uniform in respect to its rate of absorbing chlorine (which is certainly not exactly so).

Derivation of Equation for Line 4.—Let c represent the concentration of chlorine at any distance, x , a the residual chlorine capacity of the charcoal and v the rate of supply of chlorine expressed in cm. of charcoal saturated per hour in the event of complete reaction. The rate of the absorption reaction is $k \times c \times a$.

Considering a given portion of absorbing material, its residual capacity is diminishing at the rate given by:

$$\frac{\partial a}{\partial t} = -kac \quad (1)$$

Considering a given portion of air, its chlorine content is diminishing at the rate given by the equation

$$\frac{\partial c}{\partial x} = \frac{-k}{v} ac. \quad (2)$$

From this the following equations can be obtained, in which $a' = a/a_0$, $c' = c/c_0$, $x'' = 0.4343 ka_0 x/v$ and $t'' = 0.4343 kc_0 t$. (The derivation will be found in an appendix.)

$$c' = \frac{10^{x''}}{10^{x''} - 1 + 10^{t''}} \quad (23)$$

$$a' = \frac{10^{x''}}{10^{x''} - 1 + 10^{t''}} \quad (24)$$

Except for very small values of both x'' and t'' , the middle term in the denominators is entirely negligible and the equations become:

$$c' = \frac{1}{10^{x''-t''} + 1}$$

$$a' = 1 - c'$$

Line 4 of Fig. 3 represents the relation between concentration and time, as given by the first of these equations.

It should be noted that other causes will tend to "round off" the angles in the curve, notably reversibility of the absorption reaction and inhomogeneity of composition or packing of the charcoal.

5. Line 4 is a *symmetrical* curve with its point of inflection at 50% transmission. If, however, the rate of absorption falls off more rapidly than the residual capacity of the charcoal, as will be the case if the charcoal consists of 2 or more constituents of unequal reactivity, an unsymmetrical curve will be obtained. This is illustrated by Line 5.

6. In all these cases it has been assumed that the action is entirely between the charcoal and the chlorine. If, however, the charcoal acts as a catalyst¹ for reactions between the chlorine and (for example) water vapor, the transmission will reach a value lower than 100% when the chloride capacity of the charcoal has been exhausted; and if the rate of catalysis is great enough in proportion to the rate at which chlorine is being supplied, no chlorine will be transmitted, however long the experiment be continued. These cases are represented by Lines 6 and 7.

VI. Results Obtained by the Dynamic Method and the Effect of Different Variables on the Transmissions.

The reproducibility of the results is shown in Fig. 4, which represents 2 typical experiments in which both chlorine and hydrogen chloride were determined in the effluent gas. The variations are seen to be slight. They probably resulted chiefly from irregularities in packing of the charcoal in the chamber. Unfortunately, the importance of this factor was not fully realized until a large part of the work given in this paper had been done.

The effect of different variables on the transmission of chlorine and of hydrogen chloride is as follows.

1. **Kind of Charcoal.**—The strikingly great variation in absorption which is exhibited by different charcoals is illustrated in Fig. 5, showing the transmission curves of 4 different charcoals, where Specimen D is seen to have had a service time approximately 400 times that of A.

The general similarity in form of the curves suggests the process involved to be qualitatively the same for all, and the service times of various charcoals may depend more upon variations in the proportions of active to relatively inactive constituents in each than to differences between the materials as a whole.

Although the apparent densities of these charcoals vary considerably, the service times vary still more, and their order with respect to apparent density is not the same as that with respect to service time.

¹ As it is not certain whether the charcoal is permanently altered, the word "catalysis" has been used throughout this paper to include any action involving chlorine, water and charcoal and yielding hydrogen chloride (cf. Bancroft, *J. Phys. Chem.*

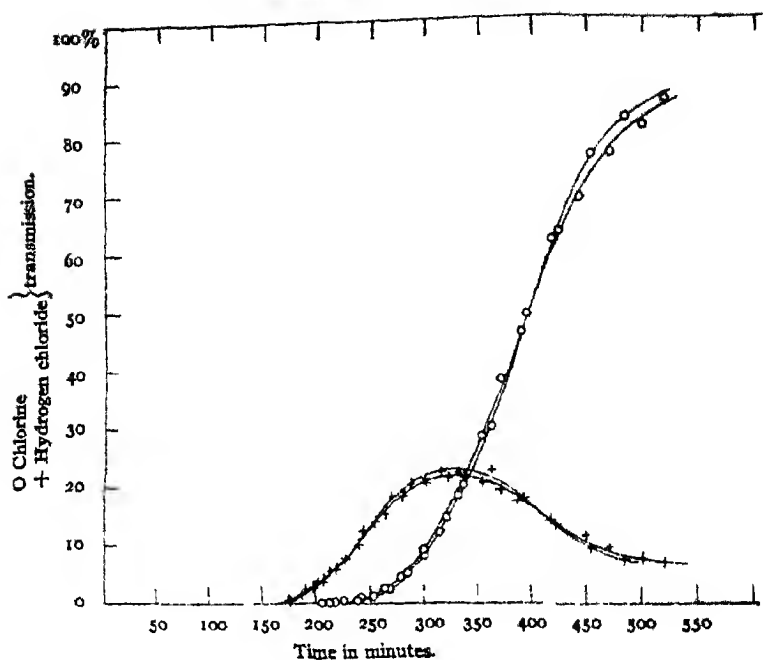


Fig. 4.

Transmission curves of dry chlorine and hydrogen.

Charcoal = E.

Depth of layer = 10 cm.

Cross-section = 10.75 sq. cm

Weight = 67.0 g.

Mesh = 8-10

Temperature = 25.0°.

Velocity of gas = 500 cm/min.

Air-chlorine ratio = 500-1.

Water content of air = 0.

Pressure of gas above charcoal = 1 atmosphere.

From a consideration of the service time of the specimens plotted in Figs. 5 and 7, which follow, it becomes evident that variations between the activities of any 2 charcoals is greater than that which would result from any reasonable variation in the humidity of the gas stream.

2. Depth of Layer.—When the layer is very thin, constituents of charcoal having a low reaction velocity do not have a marked influence on the shape of the chlorine transmission curve. As the thickness increases, however, the time factor operates to increase the importance of the less active material in the sense that doubling the depth of absorbent layer more than doubles the time required for either the front of the chlorine wave or a layer of given chlorine concentration to reach a proportional point in the charcoal column. Chlorine transmissions of the

Fig. 6. It seems probable that the increasing slant of these curves as the depth of layer becomes greater is a consequence of the peculiar effect of relatively inactive constituents discussed above.

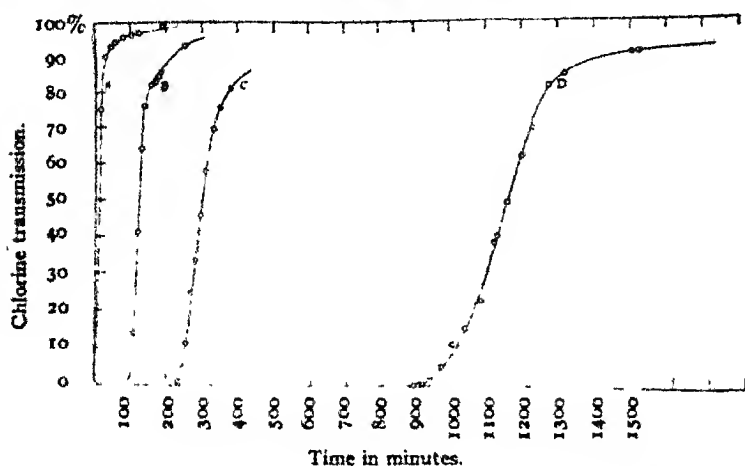


Fig. 5

Transmission curves of charcoal, A, B, C and D, with dry chlorine-air mixture.

Charcoals = A, B, C and D.

Depth of layer = 10 cm.

Cross-section = 10.75 sq. cm.

Weights. A = 23 g.; B = 77 g., C = 77 g.;

D = 66 g.

Mesh = 20-40.

Temperature = 25.0°.

Velocity of gas = 250 cm./min.

Air-chlorine ratio = 1000-1.

Water content of air = 0.

Pressure of gas above charcoal = 1 atmosphere.

3. **Water Content of the Gas Mixture.**—The extent to which chlorine was consumed by chemical action yielding hydrogen chloride was not appreciated in the earlier part of the investigation. Its great importance can be seen from Fig. 7, in which the transmission curves both for chlorine and hydrogen chloride at different humidities are shown.

The efficiency of the charcoals as catalysts for the reaction between water and chlorine and the capacity of charcoals for chlorine absorption have been found to be approximately proportional. Charcoal E, Fig. 7, which was employed in the study of the effect of gas humidity differences, had a high chlorine capacity and, therefore, was well suited to a study of catalysis.

It will be seen from the results of hydrogen chloride titrations given, that for humidity values up to 40% the courses of the reactions during the first 375 minutes were approximately the same. After this time, however, the magnitude of the catalysis was considerably dependent upon the supply of incoming moisture. This charcoal was not dried before

the experiments were begun and was probably in equilibrium with atmospheric humidity of at least 40%. The results obtained suggest that, in the absence of liquid phase, adsorbed water alone played an important part in the catalysis and if any assistance was rendered by moisture from the gas stream taking the place of that used up in the reaction, its effect was slight until after about 325 minutes. From this time on, water supplied by the gas mixture did assist the catalysis to an extent proportional to the water concentration. This is indicated by the relative positions of the hydrogen chloride curves from 500 minutes on

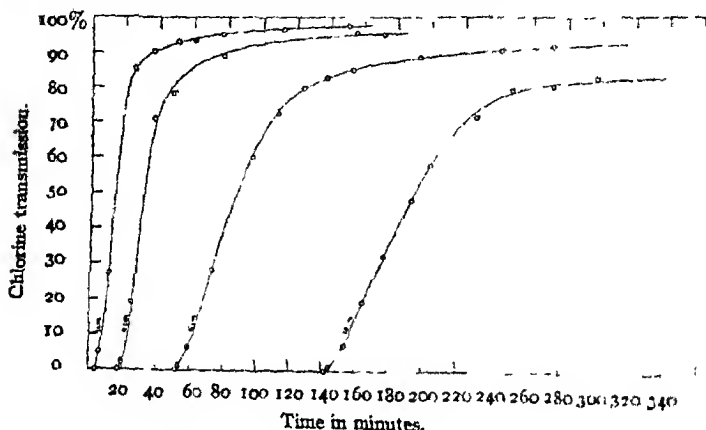


Fig. 6.

Transmission of chlorine through different depths of absorbent

Charcoal = B.

Depth of layer = 1, 2, 5 and 10 cm

Cross-section = 10.75 sq. cm

Weight = 7.7, 15.4, 38.5 and 77.0 g.

Mesh = 20-40.

Temperature = 25.0°

Air-chlorine ratio = 1000-1

Velocity of gas = 250 cm./min

Water content of air = 80.0% saturation.

Pressure of gas above charcoal = 1 atmosphere

Pressure of gas below charcoal = 1 atmosphere — 0.42, 0.69, 1.46 and 2.60 cm. H₂O

At a humidity value somewhere between 40 and 80% the affinity of adsorbed hydrogen chloride for water probably precipitated the liquid phase and this greater concentration of the water accelerated the catalysis for a certain length of time.

The late appearance of hydrogen chloride beyond the charcoal when the liquid phase was present may be attributed to the probability that the capacity of the system for hydrogen chloride was increased by the solvent action of the liquid present. The collection, in this experiment, of a strong aqueous hydrogen chloride solution at the elbow below the charcoal column as well as a distinctly wet appearance of the charcoal

itself left no doubt of the actual existence of the liquid phase. For humidity values of 50% or less no liquid was ever noticed on the charcoal surface.

It will be shown later that the capacity of Charcoal D for chlorine, leaving catalysis out of account, was increased by previous drying of the absorbent. With Charcoal E the consumption of chlorine through catalysis was not, in the earlier part of the experiments, increased by humidity

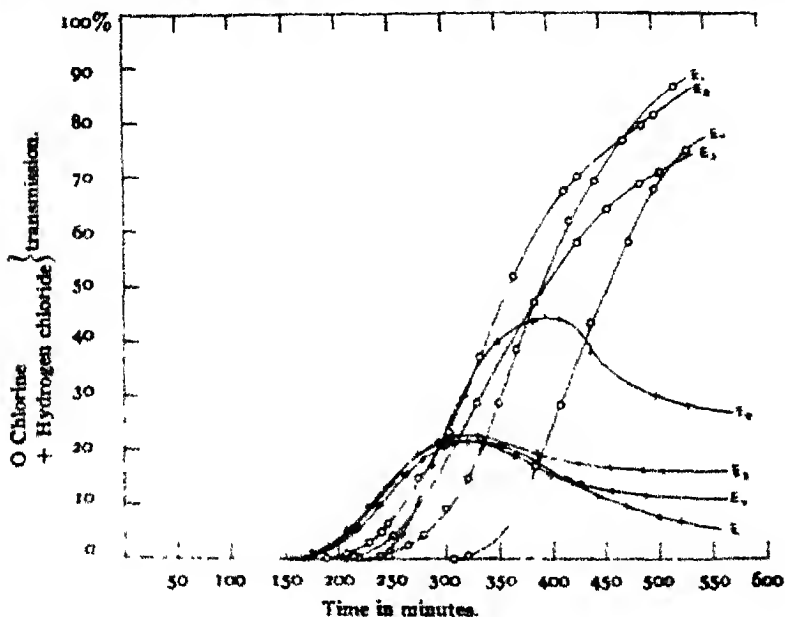


Fig. 7.

Transmission curves of chlorine and hydrogen chloride at different humidities.

Charcoal = E.

Depth of layer = 10 cm.

Cross-section = 10.75 sq. cm

Weight = 67.0 g.

Mesh = 8-10.

Temperature = 25.0°

Velocity of gas = 500 cm/min

Air-chlorine ratio = 500-1.

Water content of air: E₁ = 0.0% saturation; E₂ = 20.0% saturation; E₃ = 40.0% saturation; E₄ = 80.0% saturation.

Pressure of gas above charcoal = 1 atmosphere

values of either 20 or 40%, hence the service time of the charcoal in the gas containing those moisture concentrations was less than when dry air was used, for in the last-named case the absorbent was automatically dried. Soon after the chlorine "break," however, the moisture in the gas mixture did assist catalysis to such an extent that the chlorine titrations were relatively lower than when dry air was used, and this is re-

lected in the curves by an increasingly lower slant as the humidity concentrations go up.

At a humidity value somewhere between 40 and 80% catalysis became so great, even in the earlier part of the experiment, that it operated to lengthen the service time of the charcoal above that realized with the use of dry air. The above results indicate that a minimum service time for chlorine absorption would occur when humidity values were somewhere between 20 and 80%.¹

When the humidity was 80% the chlorine "break" was delayed but the slant of the chlorine absorption curve was steeper than for lower humidity

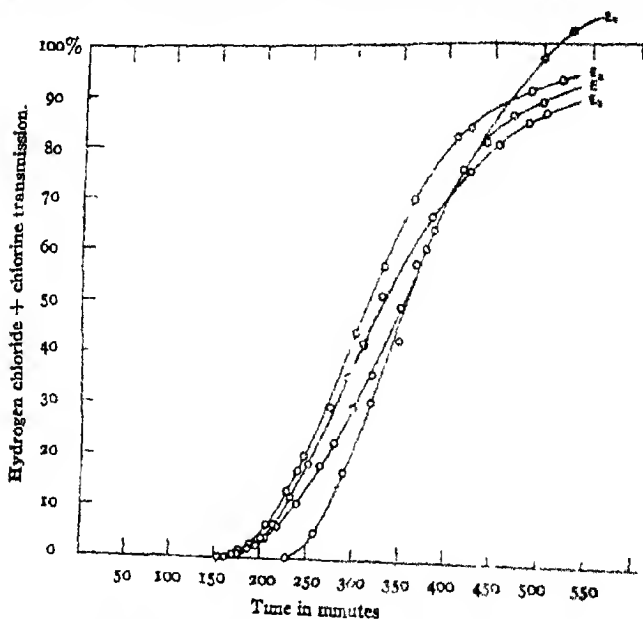


Fig. 8

Summation curves of chlorine and hydrogen chloride transmission at different humidities.

Charcoal = E.

Depth of layer = 10 cm

Cross-section = 10.75 sq. cm.

Weight = 670 g.

Mesh = 8-10

Temperature = 25.0°.

Velocity of gas = 500 cm./min.

Air-chlorine ratio = 500-1.

Water content of air: E_1 = 0.0% saturation;

E_2 = 20.0% saturation; E_3 =

40.0% saturation, E_4 = 80.0% saturation.

Pressure of gas above charcoal = 1 atmosphere.

¹ The properties of different charcoals exhibit a wide variation so this statement is intended to apply to this particular specimen only

values. This effect, peculiar to the 80% humidity experiment, is a direct consequence of the relatively more rapid decline¹ in the extent of catalysis during the time from 400 minutes onward.

The results in Fig. 8 show the sum of the transmission values of chlorine, both combined and elementary, as given in Fig. 7. For humidity values of 0, 20 and 40%, represented by E_1 , E_2 and E_3 , respectively, no pronounced differences exist. The presence of a liquid phase when 80% humidity was employed provided a reservoir for hydrogen chloride, supplying that compound to the gas stream at a rate diminishing more slowly than the rate of chlorine transmission increased. For this reason the chlorine, elementary and combined, transmitted by the charcoal, amounted at one time to more than that which entered the apparatus.

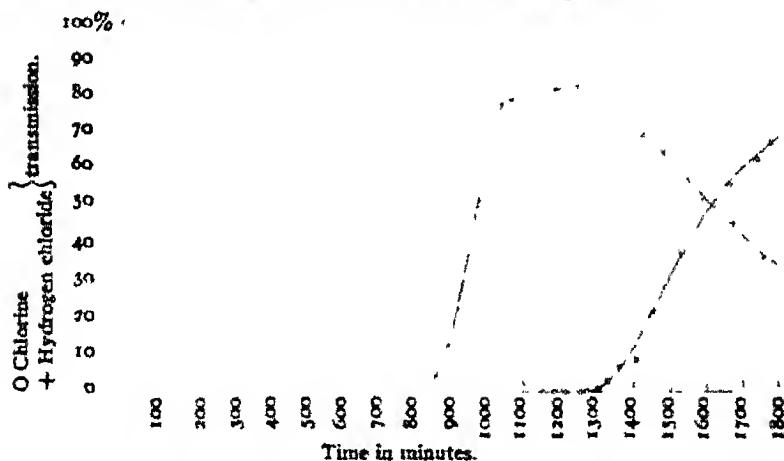


Fig. 9.

Transmission curves of chlorine and hydrogen chloride at 50% humidity and low rate of flow.

Charcoal = D.

Depth of layer = 10 cm

Cross-section = 10.75 sq cm.

Weight = 66.0 g.

Mesh = 20-40.

Temperature = 25.0°.

Velocity of gas = 250 cm./min.

Air-chlorine ratio = 1000-1.

Water content of air = 50.0% saturation.

Pressure of gas above charcoal = 1 atmosphere.

Pressure of gas below charcoal = 1 atmosphere less 2.66 cm. H_2O .

Fig. 9 shows the transmission curves of chlorine and hydrogen chloride at 50% humidity at low rates of flow. Since the experimental conditions were very different from those in the humidity experiments described above, the results are not readily comparable but are illumina-

¹ To what extent this rapid decline resulted from choking of the capillary spaces by liquid can only be conjectured, but the catalytic surface was no doubt somewhat reduced thereby.

ting. Since the lower velocity, here, of both the air and chlorine, eliminated to some extent the crowding of successive events which occurred with the higher gas velocity and chlorine concentration. This makes an analysis and interpretation of the results more easily accomplished.

During the progress of chlorine absorption by the dynamic method a relatively thin heated section travels down along the charcoal column and arrives at the bottom nearly simultaneously with the first appearance of chlorine. In the earlier experiments without a thermostat, the tube was warm to the touch for perhaps a centimeter length and at a depth below the surface of the charcoal proportional to the stage of the experiment.¹ By a consideration of this phenomenon together with the shape of the transmission curves a possible interpretation of the results in Fig. 9 may be deduced as follows

1. During the first 850 minutes all of the chlorine, as well as the hydrogen chloride, was absorbed and the warm reaction zone had progressed approximately $\frac{1}{4}$ of the length of the charcoal column.²

2. At 850 minutes the charcoal was no longer able to hold all the hydrogen chloride produced and that compound appeared in greater and greater amounts during the next 200 minutes.

3. At about 1050 minutes the charcoal had become practically saturated with respect to hydrogen chloride and from that time on for 200 minutes all of the hydrogen chloride produced and a trace of chlorine escaped.

4. After about 1300 minutes had passed, the lower edge of the active reaction zone reached the lower end of the charcoal column and as the thickness of the former became less the importance of catalysis diminished and the concentration of chlorine in the effluent gas necessarily increased.

The fact that, from 1300 minutes on, the decrease in rate of hydrogen chloride transmission balanced the increase in rate of chlorine transmission indicates catalysis amounting to practically 100% of absorbed chlorine, both before and after the appearance of chlorine beyond the charcoal. The increase in rate of chlorine supply soon places a limit beyond which complete catalysis does not occur. This is illustrated by the pronounced break in the transmission curve, Fig. 13. Here the rate of chlorine supply was 4 times that in the experiment under consideration.

5. Temperature.—As is generally recognized, the capacity of char-

¹ It was obviously impossible to observe, and *a fortiori* to measure this effect when the thermostat was employed

² The rate of movement of the rapid reaction zone down the charcoal column was probably progressively slower as time went on because a certain amount of chlorine was always being sluggishly absorbed by the charcoal in the wake of the more rapid reaction layer and the quantity of this relatively inactive material increased progressively.

coals for gases decreases as the temperature is elevated, since ordinary absorption is a reversible reaction. When water is present in an air-chlorine mixture, however, this behavior is somewhat modified because higher temperatures (within the range studied) favor the catalytic reaction¹ in which charcoal assists the interaction of chlorine and water with the formation of hydrogen chloride and oxygen. Other chlorine compounds may also have been produced but they were not detected in the exhaust gas stream.

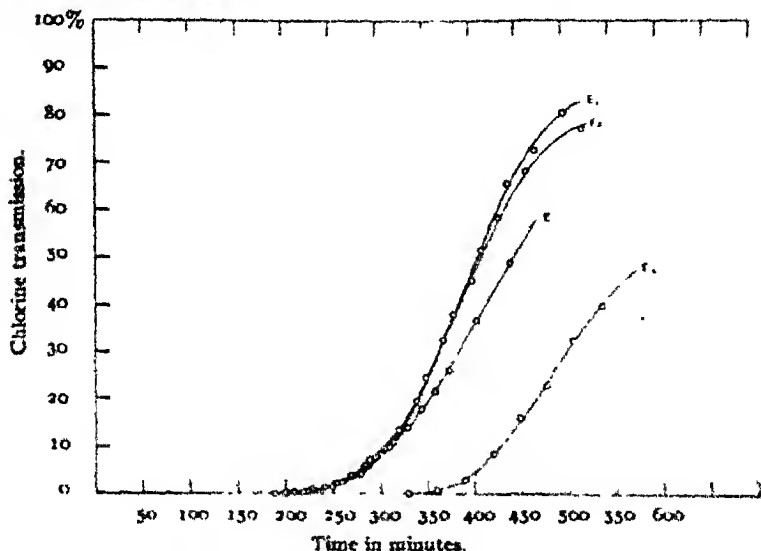


Fig. 10.

Transmission curves of chlorine at different temperatures.

Charcoal = E.

Depth of layer = 10 cm.

Cross-section = 10.75 sq. cm.

Weight = 67 g.

Mesh = 8-10.

Temperature: E₁ = 0.0°; E₂ = 17.5°, E₃ = 25.0°; E₄ = 37.5°.

Velocity of gas = 300 cm./min.

Air-chlorine ratio = 500-1.

Water content of air = 50.0% saturation.

Pressure of gas above charcoal = 1 atmosphere.

Pressure of gas below charcoal = 1 atmosphere less 0.85 cm. H₂O.

¹ By passing a rapid stream of chlorine together with an excess of steam and a small amount of air, over charcoal enveloped in a steam bath, all of the chlorine was apparently converted to hydrogen chloride for a long period of time. The water insoluble gas evolved contained a high proportion of carbon dioxide.

It is known that charcoals prepared under special conditions are often so susceptible to oxidation that they even catch fire spontaneously in air. Possibly the consumption of that portion of chlorine which appears as hydrogen chloride beyond the charcoal may be largely due to a reaction in which carbon is oxidized to carbon dioxide, the oxygen being furnished by hypochlorous acid or other oxidizing agent containing hydrogen, oxygen, and chlorine, the reduction of which yields hydrogen chloride.

Fig. 10 shows the effect of temperature on chlorine transmission. Within the temperature range studied it will be seen that the effect of equal increments of temperature is irregular. Two conflicting tendencies operate to determine the service time and the progress of absorption after the chlorine "break." The absorption capacity of the charcoal is lowered by a rise in temperature but catalysis, on the other hand, is at the same time assisted thereby. With respect to service time, the resultant of these opposing tendencies is nearly identical for the temperature range 0.0° to 12.5° . After the transmission value has reached the neighborhood of 40%, the escape of chlorine with temperature rise becomes progressively less for all temperatures used. The interval 25.0° to 37.5° is marked by a pronounced change in the service time of the charcoal with respect to chlorine.

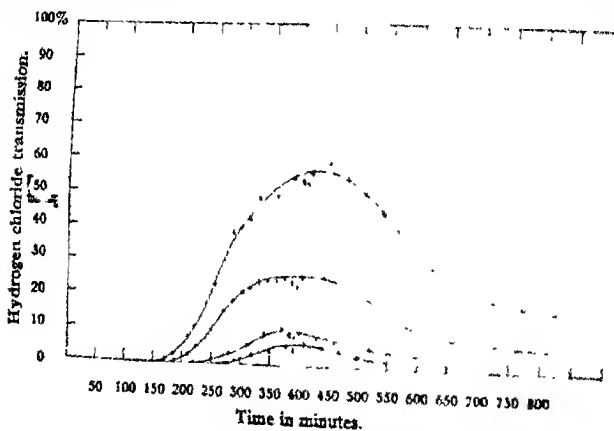


Fig. 11.

Charcoal = E.
Depth of layer = 10 cm.
Cross-section = 10.75 sq. cm
Weight = 67.0 g.
Mesh = 8-10.

Temperature: $E_1 = 0.0^{\circ}$; $E_2 = 12.0^{\circ}$; $E_3 = 25.0^{\circ}$; $E_4 = 37.5^{\circ}$.

Velocity of gas = 500 cm./min.
Air-chlorine ratio = 300-1
Water content of air = 50.0% saturation.
Pressure of gas above charcoal = 1 atmosphere.
Pressure of gas below charcoal = 1 atmosphere less 0.85 cm. H_2O .

Fig. 11 shows the effect of temperature on the transmission of hydrogen chloride. The transmission of hydrogen chloride as affected by the temperature is dependent upon 2 factors: catalysis, which increases the total quantity of that acid; and evaporation which reduces the amount of hydrogen chloride retained by the charcoal. The results of the hydrogen chloride titrations, Fig. 11, represent the resultants of these 2 effects, and the areas inclosed between the various curves, up to a given time,

measure in each case the differences in transmission. For instance, up to 450 minutes the ratio for the intervals 0.0° to 12.5° : 12.5° to 25.0° : 25.0° to 37.5° was about 1 : 5 : 8.

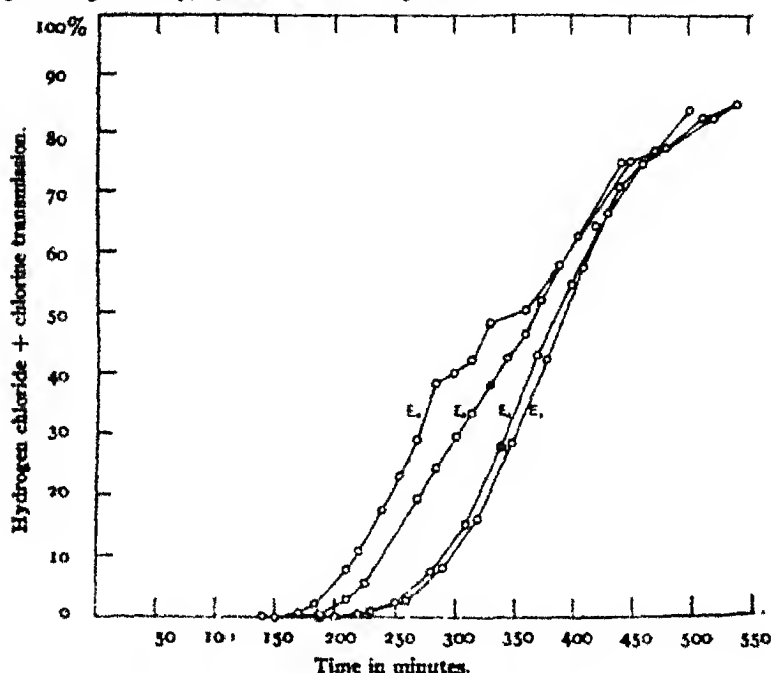


Fig. 12.

Transmission curves of chlorine and hydrogen chloride combined.

Charcoal = E.

Depth of layer = 10 cm.

Cross-section = 10.75 sq. cm.

Weight = 67.0 g.

Mesh = 8-10.

Temperature: $E_1 = 0.0^{\circ}$; $E_2 = 12.5^{\circ}$; $E_3 = 25.0^{\circ}$; $E_4 = 37.5^{\circ}$.

Velocity of gas = 500 cm/min.

Air-chlorine ratio = 500-1

Water content of air = 50.0% saturation.

Pressure of gas above charcoal = 1 atmosphere.

Pressure of gas below charcoal = 1 atmosphere less 0.85 cm. H_2O (Mean value.)

Fig. 12 depicts the relation between temperature and the transmission of chlorine and hydrogen chloride combined. Evidently temperature has surprisingly little effect on this combined transmission. To reach the 2 points, "break" and 70% total transmission, the time required is almost identical in the temperature range studied. The greatest temperature effect is to be seen at about 20% transmission and, as was to be expected, the greatest transmission, at a given time from the beginning of the experiment, occurred with the highest temperature, and so on down the scale.

Under the particular conditions of charcoal depth and chlorine flow employed in this work it was found that chlorine and hydrogen chloride (Figs. 10 and 11) appeared beyond the absorbent simultaneously when the temperature was in the neighborhood of 12.5° . Chlorine appeared sooner than hydrogen chloride below 12.5° and the order was reversed above that temperature. The apparently high temperature coefficient of charcoal for hydrogen chloride absorption probably results largely from the effect of temperature on the magnitude of charcoal catalysis whereby chlorine reacts with water, forming hydrogen chloride.

6. Pressure.—The absorption of chlorine and the catalysis of chlorine and water by charcoal were investigated at reductions of pressure of 30 and 60 cm. of water, respectively, and also at atmospheric pressure. The results in all 3 cases were found to be so similar that the slight variations which did occur may have been within the limit of experimental error. If anything, the reduction in pressure increased the efficiency of the charcoal for the removal of chlorine from the gas stream.

7. Interruption During the Course of Experiment.—Fig. 13 clearly demonstrates the effect of a period of rest on charcoal which has been saturated with chlorine and hydrogen chloride in the presence of moisture. In a 12-hour interval which elapsed between the end of the first

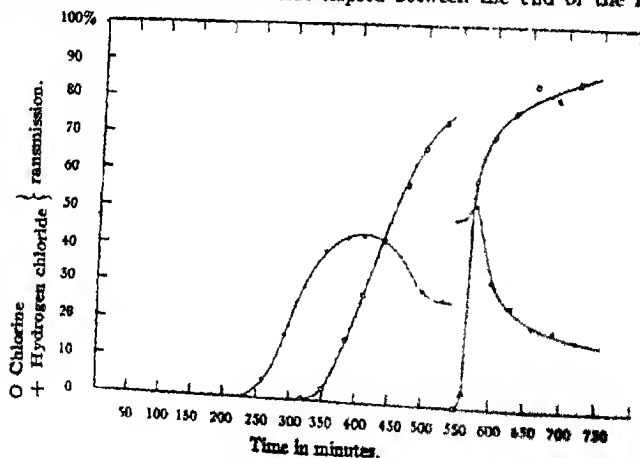


Fig. 13

Charcoal = E

Depth of layer = 10 cm.

Cross-section = 10.75 sq. cm.

Weight = 67.0 g

Mesh = 8-10

Temperature = 25.0°

Velocity of gas = 500 cm./min.

Air-chlorine ratio = 500-1.

Water content of air = 80.0% saturation.

Pressure of gas above charcoal = 1 atmosphere

Pressure of gas below charcoal = 1 atmosphere less 0.91 cm. H_2O .

545 minute period and the resumption of the experiment all of the chlorine had either reacted with water to form hydrogen chloride or become so firmly attached to the charcoal that it could not be dislodged by the air stream. The former seems the more plausible reason for the observed phenomenon, because the quantity of hydrogen chloride transmission immediately after the intermission was usually large. The capacity of the absorbent for chlorine had not revived very much, however. This may have been due to the fact that the available secondary valence forces (or whatever the forces are which cause absorption) were largely satisfied by hydrogen chloride, water, and firmly held chlorine. It follows from the assumption that an intermission is accompanied by catalytic conversion of chlorine to hydrogen chloride that a reduction in the rate of chlorine flow would result in a larger proportion of the entering chlorine being converted to hydrogen chloride or other chlorine compounds; at least if the catalytic efficiency of the charcoal were not impaired.¹

VII. Data Obtained by the Static Method.

Fig. 14 represents transmission curves of 4 charcoals where time is plotted against chlorine absorption per g. of charcoal. The differences between B, C and D seem to be of degree rather than of kind, whereas

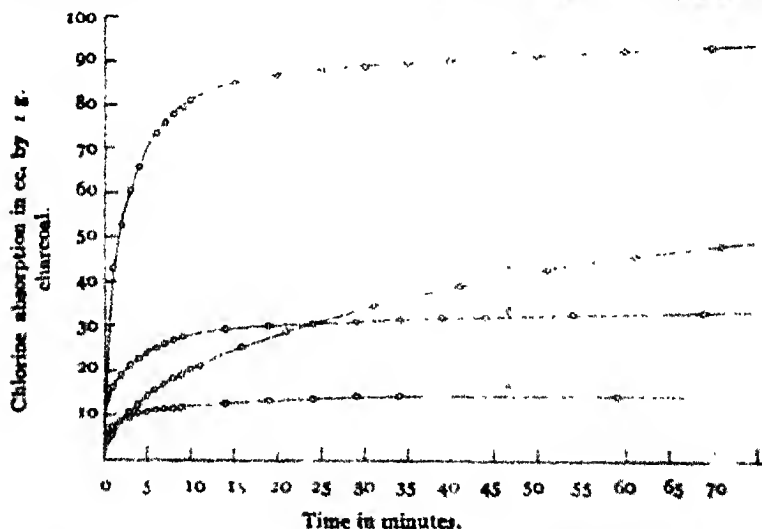


Fig. 14.

Charcoals = A, B, C and D. Mesh = 10-70. Temperature = 24.0°.

¹ Reducing the rate of chlorine flow not only automatically increases the ratio of water to chlorine—the rate of air flow remaining constant—but it also approaches the state of rest under which conditions all uncombined chlorine has been shown to react to form hydrogen chloride or other chlorine compounds.

the nature of Curve A suggests that charcoal to be of an entirely different type. This is to be expected from the data given in Section IV above.

VIII. Revivification by Heating in Vacuo.

The chlorine capacity of Charcoal D¹ was increased by one exposure to chlorine followed by heating to dull redness *in vacuo* (see D_a and D_b, Fig. 15). This was at least partly due to the fact that before the first exposure to pure chlorine, places to which this gas would otherwise have been fastened were already occupied by other chemical individuals.

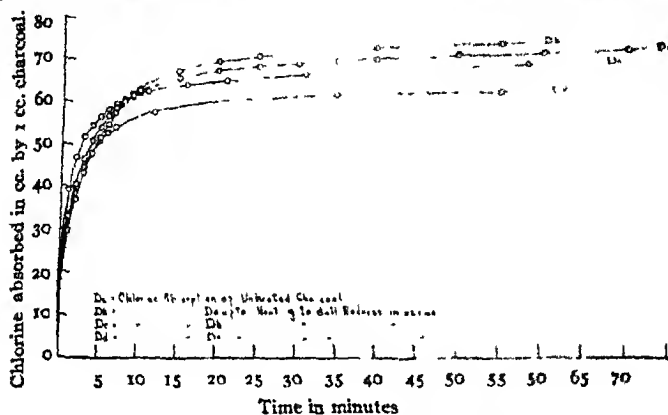


Fig. 15

Charcoal = D Mesh = 10-20 Temperature = 24.0°

That is to say, the absorbing surface was relatively clean with respect to absorbed material at the beginning of the second exposure

TABLE I.

Change in wt.	From	To	%
Loss.....	D _a	D _b	1.21
Gain...	D _b	D _c	4.75
Gain..	D _c	D _d	16.62

It is also possible that chlorine may have formed volatile compounds with certain inactive constituents of the charcoal whose disappearance during later evacuation left a material containing a higher proportion of active absorbent and a material more thoroughly honeycombed by capillary spaces suitable for absorption. The loss in weight shown in Table I at least does not conflict with this hypothesis. ² This charcoal gained weight after several exposures to chlorine, but this may have resulted from the chlorination or oxidation of carbon complexes with high molecular weight which reacted sluggishly from the standpoint of absorption.

¹ Before the first exposure to chlorine this charcoal was allowed to come to equilibrium with water and other gases in the atmosphere of the laboratory.

3. The curves indicate that after several exposures the chlorine capacity of the charcoal had been slightly reduced but the steep rise during the earlier part of the experiment shows that the activity was not seriously impaired.

IX. Appendix.

Given

$$\frac{\partial c}{\partial x} = -\frac{k}{v} ac \quad (1)$$

$$\frac{\partial a}{\partial t} = -kac. \quad (2)$$

For discussion and definitions, see text immediately preceding Equations 1 and 2 in Section V.

Now, the "boundary conditions" are that the charcoal has initially a uniform volume chlorine capacity, which we will call a_0 , and that the air entering the charcoal has a constant chlorine concentration, which we will call c_0 .

Let

$$a' = a/a_0, \quad c' = c/c_0, \quad x' = kn_0x/v, \quad t' = kt_0t.$$

Then:

$$\frac{\partial c'}{\partial x'} = -a'c' \quad \frac{\partial a'}{\partial t'} = -a'c', \quad (3) \quad (4)$$

Or

$$\frac{\partial \ln c'}{\partial x'} = -a' \quad \frac{\partial \ln a'}{\partial t'} = -c'. \quad (5) \quad (6)$$

When $t' = 0$, $a' = 1$, and (5) integrates to

$$c' = e^{-x'}. \quad (7)$$

Where $x' = 0$, $c' = 1$, and (6) integrates to

$$a' = e^{-t'}. \quad (8)$$

Differentiating (5) and (6)

$$\frac{\partial^2 \ln c'}{\partial t' \partial x'} = -\frac{\partial a'}{\partial t'} = a'c' \quad \frac{\partial^2 \ln a'}{\partial x' \partial t'} = -\frac{\partial c'}{\partial x'} = a'c'. \quad (9) \quad (10)$$

Subtracting (10) from (9)

$$\frac{\partial^2 \ln (c'/a')}{\partial t' \partial x'} = 0 \quad (11)$$

$$\ln (c'/a') = f(x') + f(t'). \quad (12)$$

Imposing boundary conditions this becomes

$$\ln (c'/a') = t' - x' \quad (13)$$

Or

$$c'/a' = e^{t'-x'}.$$

Rewriting (3) and (4)

$$-\frac{\partial c'}{\partial x'} = \frac{a'}{c'} = e^{x'-t'} \quad -\frac{\partial a'}{\partial t'} = \frac{c'}{a'} = e^{t'-x'}. \quad (15) \quad (16)$$

Integrating

$$1/c' = e^{x'-t'} - f(t') \quad 1/a' = e^{t'-x'} - f(x'). \quad (17) \quad (18)$$

Evaluating the constants, from (7) and (8)

$$1/c' = e^{x'-t'} - e^{-t'} + 1 \quad 1/a' = e^{t'-x'} - e^{-x'} + 1, \quad (19) \quad (20)$$

Or

$$c' = \frac{e^{t'}}{e^{x'-t'} - 1 + e^{t'}} \quad a' = \frac{e^{x'}}{e^{t'-x'} - 1 + e^{x'}}. \quad (21) \quad (22)$$

Placing $x'' = 0.4343 x'$ and $t'' = 0.4343 t'$ and changing to common logarithms

$$c' = \frac{10^{t''}}{10^{x''} - 1 + 10^{t''}} \quad a' = \frac{10^{x''}}{10^{t''} - 1 + 10^{x''}}. \quad (23) \quad (24)$$

X. Summary.

1. In the particular series of charcoals here considered the variations in chlorine-absorbing power between any 2 kinds was greater than that which would result from any attainable variation in the humidity of the gas stream.

2. The order of the charcoals with respect to duration of complete chlorine absorption¹ is not the same as that with respect to apparent density.

3. The duration of complete chlorine absorption increases more rapidly than the thickness of the layer of charcoal, other conditions remaining constant.

4. For the charcoals studied the duration of complete chlorine absorption passes through a *minimum* for a relative humidity in the neighborhood of 50%.

5. The duration of complete chlorine absorption is at a *minimum* between 0° and 12.5°.

6. For the charcoals studied, below 12.5° chlorine appeared beyond the charcoal before hydrogen chloride; above 12.5° hydrogen chloride appeared before chlorine.

7. Reductions in pressure up to two feet of water (barometric pressures down to 71 cm. mercury) have little effect.

8. The chlorine capacity of the charcoal studied is increased by one exposure to chlorine followed by heating to dull redness *in vacuo*.

WASHINGTON, D. C.

¹ Defined as above as the "service time" of the charcoal.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE VAPOR PRESSURES OF CADMIUM, LEAD AND TIN AMALGAMS.

BY JOEL H. HILDEBRAND, A. H. FOSTER AND C. W. BEEBE

Received January 15, 1920

The work here presented is part of a series of measurements which has been carried out during recent years upon the vapor pressures of amalgams. The previous papers give vapor-pressure measurements upon the following amalgams: zinc,¹ silver,² gold,³ bismuth,³ thallium,³ and supplement the important investigations of T. W. Richards⁴ and G. A. Hulett⁵ and their co-workers upon the electromotive forces of amalgam-concentration cells and other properties of amalgams at ordinary temperatures.

The experimental procedure was essentially the same as that used in the earlier investigations and need not be again described. The accuracy is somewhat inferior to that of earlier measurements, although the "probable error" of the average value at each concentration is less than ± 0.001 in all cases except with the concentrated lead amalgams, where, for some unknown reason, it increased.

The results are given in Tables I, II and III, where n represents the number of mols. of mercury per mol. of the other constituents, N represents the mol-fraction of mercury (equal to $n/(n+1)$); p the vapor pressure of mercury over the amalgam of composition N , and p_0 that of pure mercury at the same temperature.

The calculated values were obtained by the aid of the equation

$$\log p/p_0 = \log N + a/(1 + cn)^2 \quad (1)$$

using the following values of a and c :

	Cd-amalgams	Pb-amalgams	Sn-amalgams
a	-1.40	+0.252	+0.220
c	+1.90	+0.31	+0.26

This equation is to be regarded simply as an empirical expression for smoothing vapor-pressure data, as was done in the earlier papers of this series.

The results are also expressed graphically by the curves in the figure. It will be noted that the vapor pressures of cadmium amalgams are less than are demanded by Raoult's law, $p/p_0 = N$, and that the deviation becomes much greater at high concentrations of cadmium. Tin and lead

¹ J. H. Hildebrand, *Orig. Comm. 8th Inter. Cong. Appl. Chem.*, 22, 139, 147; *Trans. Am. Electrochem. Soc.*, 22, 319, 335 (1912); *THIS JOURNAL*, 35, 501 (1913).

² Ermon D. Eastman and J. H. Hildebrand, *THIS JOURNAL*, 36, 2020 (1914).

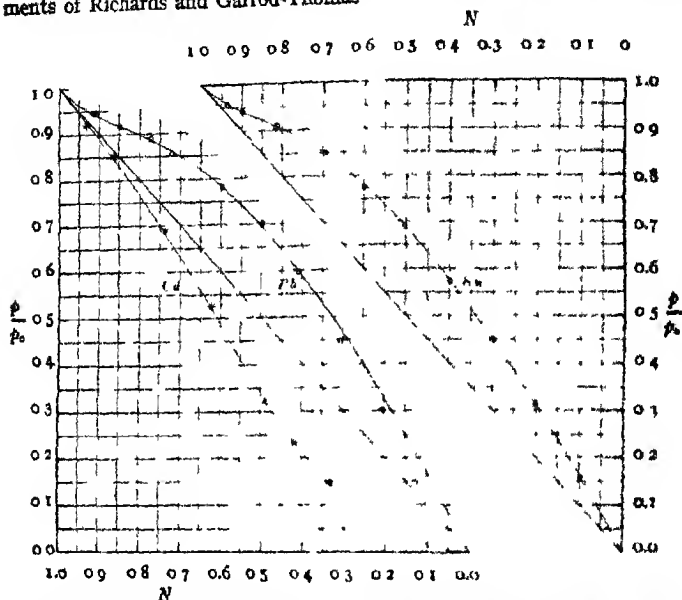
³ *Ibid.*, 37, 2452 (1915).

⁴ *Carnegie Inst. Pub.*, 36, 118; *Z. Physik. Chem.*, 58, 683 (1907); 72, 129, 165 (1909); *THIS JOURNAL*, 42, 1732 (1919).

⁵ *THIS JOURNAL*, 30, 1812 (1908); *J. Phys. Chem.*, 14, 158 (1910).

JOEL H. HILDEBRAND, A. H. FOSTER AND C. W. SEEBE.

amalgams at 324° show almost identical deviations from Raoult's law, just as they do at ordinary temperatures, as seen from the e. m. f. measurements of Richards and Garrod-Thomas



The values for lead amalgams of high lead content are very unsatisfactory, so far as consistence is concerned, and, from theoretical considerations, are doubtless too low. It is extremely improbable that the curve contains any inflection at the lower end, as the measurements would seem to demand. There is no other case known to us in all the literature on vapor pressure where such behavior is indicated. More careful investigation of this region was prevented by the entrance of all of us into war service, and it has not since seemed worth while to hold up the publication of these results for the experimental work it would require.

TABLE I—CADMIUM AMALGAMS AT 322°.

Wt. Cd G	Wt. Hg G	n	N.	Number of obs.	Obs.	p/p_0 Calc (1).	p/p_0 Calc (2)
1.046	25.23	13.51	0.931	6	0.920	0.927	0.928
2.050	22.61	6.19	0.861	5	0.850	0.845	0.847
4.752	23.90	2.815	0.738	6	0.688	0.660	0.682
7.034	20.67	1.650	0.623	6	0.525	0.522	0.513
8.874	15.10	0.953	0.488	5	0.322	0.323	0.317
8.879	11.36	0.720	0.418	6	0.232	0.235	0.233
-	-	-	0.311	6	0.148	0.148	0.154

TABLE II.—LEAD AMALGAMS AT 324°.

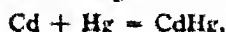
Wt. Pb. G.	Wt. Hg. G.	n.	N.	Number of obs.	p/po.	
					Obs.	Calc.
1.155	11.67	10.43	0.912	4	0.944	0.943
1.240	11.77	9.80	0.907	5	0.944	0.938
1.734	9.358	5.56	0.848	5	0.915	0.918
3.005	11.11	3.48	0.777	5	0.897	0.887
3.026	9.990	3.41	0.774	8	0.887	0.886
2.590	6.440	2.57	0.720	7	0.855	0.861
4.449	6.432	1.492	0.599	6	0.782	0.784
5.603	5.350	0.987	0.497	9	0.700	0.698
6.880	4.358	0.820	0.407	7	0.597	0.590
8.059	3.426	0.440	0.305	6	(0.448)*	0.478
8.037	3.210	0.412	0.292	4	(0.452)	0.461
9.652	2.342	0.251	0.201	9	(0.302)	0.331
7.846	1.087	0.1513	0.125	9	(0.149)	0.212
10.518	1.145	0.1122	0.101	4	(0.137)	0.174

* The values in parentheses are regarded as inaccurate.

TABLE III.—TIN AMALGAMS, AT 324°.

Wt. Sn G.	Wt. Hg G.	n	N.	Number of obs.	p/po.	
					Obs.	Calc.
0.6166	15.33	14.68	0.936	5	0.958	0.959
1.224	18.59	9.00	0.900	7	0.944	0.944
1.224	18.46	8.93	0.899	5	0.943	0.942
2.510	19.12	4.51	0.818	6	0.908	0.912
2.501	19.25	4.300	0.811	5	0.911	0.908
3.322	13.00	2.281	0.695	5	0.850	0.849
4.739	12.03	1.500	0.600	5	0.777	0.780
5.234	8.930	1.007	0.502	6	0.690	0.690
5.235	5.846	0.660	0.398	6	0.574	0.575
5.742	4.138	0.428	0.299	8	0.450	0.451
6.904	2.915	0.250	0.200	7	0.313	0.312
8.851	1.651	0.1103	0.099	4	0.159	0.160

The values for cadmium amalgams can be reproduced very closely by assuming partial solvation, according to the equation:



as was done in a previous paper,¹ for the sake of calculating the e. m. f. of cadmium amalgam concentration cells.

The formula there given was

$$\frac{p}{p_0} = \frac{n-1 + \sqrt{(n+1)^2 - 4Bn}}{n+1 + \sqrt{(n+1)^2 - 4Bn}}, \quad (2)$$

where B is a constant which is a function of the equilibrium constant for the above reaction. The values in the last column of Table I, designated "calc. (2)," have been calculated using this formula, assigning to B the

¹ J. H. Hildebrand, "The Constitution of Certain Liquid Amalgams," *This Journal*, 38, 501 (1913).

NOTE.

value 0.75, which does not differ greatly from the value 0.667, used to calculate the e. m. f. values of Richards and Forbes and of Hulett and DeLury¹ at 25°. The behavior of cadmium amalgams may, therefore, be explained on the basis of the formation of a new molecular species without assuming the failure of Raoult's law

This cannot so easily be done, however, in the cases of lead and tin amalgams, for the deviations from Raoult's law are here so great that they could be accounted for only by the assumption of molecules of lead and tin more complex than Pb_2 and Sn_2 , and even curves so calculated would not correspond at all well to the actual curves.²

A theoretical discussion of all the data on amalgams obtained in this series of investigations will be the subject of a future communication.

Summary.

1. Vapor pressures of mercury over amalgams of cadmium, lead and tin at 324° have been measured at intervals covering the entire range of concentrations.

2. The values of the constants in an empirical equation relating vapor pressure to composition are given for each amalgam

3. Cadmium amalgams gave vapor pressures less than Raoult's law demands, and the deviations can be calculated on the assumption of partial solvation, varying with the concentration according to the mass law, to form molecules of $CdHg$

4. Lead and tin amalgams give vapor pressures which are nearly equal, and are much greater than Raoult's law demands. The deviations cannot be accounted for by assumption of any simple molecular change

BERKELEY, CAL.

NOTE.

Correction.—In the paper on "The Genesis of Petroleum as Revealed by its Nitrogen Constituents," in the October, 1919, number of *THIS JOURNAL*, p. 1692, on line 32, the words "methyl chinolines" should read alkyl chinolines, and on p. 1694, on line 35, the words "12 kg." should read 3 kg.

C. F. MABERY.

¹ *Loc. cit.*

² See discussion of bismuth amalgams, *loc. cit.*

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA.]

THE FUNCTION OF VITAMINES IN THE METABOLISM OF *SCLEROTINIA CINEREA*.^{1,2}

BY J. J. WILLAMAN.

Received October 6, 1919

I. Introduction.

In the spring of 1918 the writer began an investigation of some of the biochemical phenomena concerned in the parasitism of certain phytopathogenic fungi. *Sclerotinia cinerea* (Bon.) Schröter was selected as a good subject to begin with, since it is both a virulent parasite and a ready saprophyte, and undergoes its principal life history phases under cultural conditions in the laboratory. It was proposed to begin at the very bottom, and to ascertain first the bare fundamentals of its nutrition, since most questions of parasitism must in the last analysis be referred to the nutrition of the fungus. The mechanism of penetration of the host, the mechanical and chemical equipment of the latter for warding off the attacking fungus, are in many cases of parasitism more or less secondary to the primal question, does the host furnish the necessary nutrients for the particular fungus in question? It was, therefore, thought desirable to make a preliminary study of the fundamental nutritional requirements of *Sclerotinia*, the brown-rot organism of drupe and pome fruits.

Currie³ has come the nearest to making this sort of a study. Using *Aspergillus niger*, he found that the only ions required are potassium, magnesium, sulfate and phosphate (PO_4^{+++}); calcium and iron, at least in so far as it is possible to exclude them from a medium by the most careful methods of purification, are not essential. Nitrogen from almost any mineral or organic form will serve. By varying the proportions of the mineral elements, nitrogen, and sugar, Currie could induce profound changes in the metabolism of this fungus, as measured by the by-products. The organism grows luxuriantly on a medium containing only the most highly purified salts, sucrose, and nitrate; it also thrives on practically all dead plant tissues and on many animal tissues; and it will readily attack and live on many living tissues, especially fruits, roots, and tubers. In other words, *Aspergillus* can run the gamut from parasitism to saprophytism.

When Currie's solutions were tried with the brown-rot fungus, failure was met with at every combination of pure salts and sugar. Pure organic

¹ Published with the approval of the Director as Paper No. 181, Journal Series, Minnesota Agricultural Experiment Station.

² This paper was submitted to the Ogden Graduate School of the University of Chicago as a thesis in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

³ J. N. Currie, *J. Biol. Chem.*, 31, 13 (1917).

nitrogen compounds, such as asparagine and amino acids, did not improve the media. When, however, a small amount of prune, peach, or apple juice was added to them, the fungus grew at a normal rate. Decoctions from other plant materials were tried, with similar results. It was apparent that *Sclerotinia* had very different nutritional requirements from those of *Aspergillus*, and that some substance, or substances, was furnished by natural materials that were essential to the growth of the fungus. A long list of nitrogen compounds, sugars, pectin, inorganic salts, and salts of organic acids, under various conditions of acidity, temperature, and light, were tried, but in all cases where the substances involved were pure, and were not contaminated by mother liquor from a plant juice, growth either did not take place or was very weak. The writer presented these data before the Cleveland meeting of the American Chemical Society in September, 1918,¹ and at that time postulated that, for the proper growth of this fungus there is required, besides suitable mineral, nitrogen, and carbohydrate food, some accessory nutrients, which are furnished by plant materials, and especially by the natural hosts of the organism. Work had not progressed far enough at this time, however, to furnish any idea as to the nature of these accessory substances. When the writer took this problem to the University of Chicago in April, 1919, Dr. William Crocker immediately suggested a comparison with the work of Williams² on the vitamine requirement of baker's yeast. The latter had found that the yeast was dependent for normal growth on an adequate supply of a water-soluble vitamine in the medium, and that this vitamine was probably identical with the antineuritic vitamine B of animal nutrition.

When *Sclerotinia* was transferred on to media containing vitamine preparations from yeast and from wheat embryo³ practically normal growth took place. The present paper deals with the further investigations of the vitamine requirements of *Sclerotinia cinerea*.

II. The Vitamines.

A brief review of the literature on vitamins insofar as it pertains to the work in hand follows.

There have been many arguments for and against the continued use of the term vitamine, principally on the basis of its implied amine structure, the proof of which has not as yet been satisfactorily established. However, the term "vitamine" is so convenient, and it is so widely used in both the scientific and the popular vernacular, that its continued use has much to recommend it, provided its meaning is generally understood and

¹ J. J. Willaman, *J. Ind. Eng. Chem.*, 10, 863 (1918).

² R. J. Williams, *J. Biol. Chem.*, 38, 463 (1919).

³ The yeast vitamine was very kindly furnished by Dr. R. J. Williams, at that time student in the University of Chicago, and the wheat embryo vitamine by Prof. R. A. Dutcher of the University of Minnesota.

accepted. In the present paper the writer uses the term "vitamine" in the sense of the following definition: *Vitamines constitute a class of substances the individuals of which are necessary for the normal metabolism of certain living organisms, but which do not contribute to the mineral, nitrogen, or energy factors of the nutrition of those organisms.* This definition (1) does not assign any specific function to the vitamins, hence it will include the substances which may prevent disease, promote growth and reproduction, cause dormancy by their temporary absence, or affect any other phase of metabolism; (2) does not limit vitamins to either plant or animal organisms; (3) does not claim that a given metabolic activity, such as growth, will not take place in the absence of the vitamins, but that it will not take place normally; (4) does not imply anything as to the nature, properties, composition, or number of the vitamins; (5) does not exclude, but actually invites the use of the terms "vitamine A," "vitamine B," "vitamine C," and so on *ad libitum*, provided this specific use of the word is specifically defined in each case. "Vitamine" then is a generic term, like "carbohydrate" and "salt." The writer has taken pains to establish this meaning of the word as it is used in the following pages, so that his free and unqualified use of it will not be misunderstood. He also submits it to the critical consideration of others.

It has been established beyond all doubt that the higher animals are dependent on plant sources for their vitamins. This is at least the case for the 3 such vitamins so far described, the growth-promoting, fat-soluble A, the antineuritic B, and the antiscorbutic C. What the function of these substances in plants is has not been touched upon at all by investigators. Other vitamins for animals may be discovered by further research; and whether these will also be phytogenic can only be conjectured.

Certain of the plants themselves may have exogenous vitamins. Bottomley, in his well-known work on bacterized peat, isolated substances which aided materially in the normal development of a number of seed-plants. In some cases very small quantities of his preparations had marked stimulative properties when used as a fertilizer. The vitamins, which he called "auximones," were produced by the action of certain soil organisms on peat and are apparently connected with nitrogen fixation. The auximones, like vitamin B, were precipitated by phosphotungstic acid and by silver nitrate. Other investigators have corroborated Bottomley's results in some cases, but have failed to do so in others. A few papers by Bottomley and others are cited for further reference.¹

¹ W. B. Bottomley, *Proc. Roy. Soc. (London)*, 88B, 237 (1914); *Ann. Botany*, 28, 331 (1914); *Proc. Roy. Soc. (London)*, 89B, 481 (1917); D. H. Jones, *Abstracts Bot.*, 1, 43 (1917); G. D. Knox, "The Spirit of the Soil," 1916, London; O. Rosenheim, *Biochem. J.*, 11, 7 (1917).

Appleman¹ believes that potato tubers contain growth-promoting substances which are essential for the proper growth of sprouts. These substances are present in limited amounts; hence, his recommendation for a minimum size of seed piece in cutting tubers for seed purposes. He ascribes the "spindling sprout" disease of potato tubers to a low content of these growth-promoting substances.

Among the fungi other examples of vitamine requirements have been brought to light. Williams² found that baker's yeast is absolutely dependent on a supply of vitamine in the medium in which it is to grow. He could use the rate of multiplication of a single yeast cell in hanging drop culture as an index of the vitamine content of the medium. A single cell in a purely synthetic medium would fail to grow. If many cells were present, they became less sensitive to a lack of vitamine until, if a mass of yeast "as big as a pin head," as recommended by Pasteur, were used in a flask of purely synthetic medium, growth would proceed normally for a time without the addition of vitamine, ultimately, however, coming to a standstill. This indicates some accommodation on the part of the yeast to small amounts of vitamine. Williams isolated the vitamine from wheat embryo, milk, pancreatin, beer wort, and autolyzed yeast, and since these are typical sources of vitamine B in animal feeding experiments, he considered the yeast vitamine to be identical with the water-soluble B. It is interesting to point out in this connection that Harden and Zilva³ found no vitamine B in beer, as measured by feeding tests with pigeons. Apparently the growth of the yeast in fermenting the beer had removed the bulk of the vitamine.

There are many examples in the literature of the ability of fungi and bacteria to grow on synthetic media with apparently no source of vitamine whatsoever. The most extreme of these media are those of Doryland⁴ and of Pieper, *et al.*⁵

But in none of these cases has the growth of a single spore or bacterium been tried; and a loopful of the previous medium, or several hundred spores, may furnish an initial supply of vitamine sufficient to maintain the organism. Thus we do not know the real relation of any of these organisms to a vitamine supply.

Several instances of vitamins for bacterial growth are on record. Davis⁶ reports that the influenza bacillus requires, besides the protein and mineral factors of its nutrition, two substances in very small amounts.

¹ C. O. Appleman, *Agr. Exp. Sta., Md., Bull.*, 212 (1918), *Science*, N. S., 48, 319 (1918).

² R. J. Williams, *J. Biol. Chem.*, 38, 465 (1919).

³ A. Harden and S. S. Zilva, *J. Inst. Brewing*, 24, 197 (1918).

⁴ C. J. T. Doryland, *J. Bact.*, 1, 135 (1916).

⁵ E. J. Pieper, C. J. Humphrey and S. F. Acree, *Phytopath.*, 7, 214 (1917).

⁶ D. J. Davis, *J. Infec. Dis.*, 21, 392 (1917); 23, 248 (1918).

One of them is hemoglobin and the other is a vitamine-like substance, as yet unidentified, which is elaborated by a number of other bacteria when grown in the same culture with the influenza bacillus, and which can also be isolated from many animal tissues and from potatoes, carrots, and sprouted rice and wheat. There is evidence that the second factor is required to make the iron of the hemoglobin available. In fact, Davis suggests a possible role for other vitamins in making available iron, calcium, phosphorus, iodine, and amino acids. Miss Lloyd¹ maintains that such is the function of the vitamins for the meningococcus. This organism must have amino acids in its nutrition, but it is unable to obtain them from proteins unless the vitamins, which it obtains from body fluids, are present.

Shearer² found "an accessory food factor" in the nasal secretion, which greatly stimulates the growth of meningococcus, pneumococcus, *B. typhosus* *B. coli communis*, some fecal streptococci, and some throat bacteria. He did not demonstrate that the substance was absolutely essential to the normal growth of the organisms, but simply that it greatly stimulated their growth; hence his substance may or may not fall under our definition of a vitamine.

Pacini and Russell³ report that the typhoid bacillus elaborates a vitamine in cultures, that the vitamine, when extracted from the cultures with alcohol and then with water, will promote the growth of experimental animals and that it is a clinical observation that patients recovered from an attack of typhoid often experience a marked acceleration in growth. Their feeding experiments cover too short periods, however, to be thoroughly convincing.

In summary of the present status of the studies of vitamins, it may be said that they are no doubt very widely distributed in both animals and plants; that in some cases plants obtain their vitamins from other plants, in some cases animals obtain theirs from plants, and in other cases plants from animals; that the best known vitamins are the A, B and C vitamins in the nutrition of higher animals; and that these vitamins have their origin in plants, but that their function there is unknown.

III. Methods Employed.

Description of *Sclerotinia* in Cultures.

Only the Monilia stage of the fungus appears in culture; that is, the mycelial felt, bearing the asexual spores, or conidia. On certain media and under certain conditions microconidia appear,⁴ but the characteristic life cycle on cultural media is the growth of the mycelium and then the

¹ D. Lloyd, *J. Path. Bact.*, 21, 113 (1916).

² C. Shearer, *Lancet*, 1917, p. 39.

³ A. J. P. Pacini and D. W. Russell, *J. Biol. Chem.*, 34, 43 (1918).

⁴ W. D. Valleau, *J. Agr. Res.*, 5, 365 (1915).

production of the conidia. In this paper these two phases will be spoken of as vegetative growth and reproduction, without qualification.

The juice of peach, plum, prune, or apple is probably one of the best and most normal medium for the laboratory propagation of this fungus. There is a certain range of dilution of such juices for optimum growth; too concentrated or too dilute juices, especially the former, will check the growth entirely. Within 24 hours after inoculation with spores on the surface of the medium, a white, cottony growth can be seen. This rapidly spreads along the surface, at the same time sending hyphae into the solution. The central or older portion of the mat becomes very dense and felty, while the rim is thinner. A normal rate of growth is almost a centimeter a day in diameter for 5 or 6 days, and then considerably slower as the limits of the containing flask and the exhaustion of the medium are approached.

The greater bulk of the mycelium is contained in the now leathery mat, very few hyphae, especially from the older portion, extending down into the medium. The surface layers are white, while beneath this the mycelium is black. The medium always contains a gel of calcium pectate coagulated by the pectase secreted by the fungus. Depending on the concentration of the pectins, this gel varies from a little flocculent precipitate to a completely solid medium; and a portion of this gel is emmeshed by the hyphae and made a part of the mycelium, as has been reported on briefly by the writer.¹

The spores may appear any time from the second to the sixth day. They may cover an area a centimeter in diameter, they may appear in scattered areas or circles, or they may cover practically the entire surface of the mat with a dense buff-colored mass. On a healthy mycelium these spores persist and remain virile for some time, at least for 2 or 3 weeks; while on unhealthy mycelium they may shrivel up within 4 or 5 days.

Both vegetation and reproduction apparently depend almost entirely on the character of the medium; they will take place in either light or darkness, and at temperatures at least from 15° to 35°, although the writer has not made any special attempt to determine the temperature limits or the formative effect of light, except insofar as to prove that they did not need to be taken into account in the present work.

Culture Methods.

100 cc. Erlenmeyer flasks, containing 25 cc. of culture solution, and incubated at 30° ± 1°, were used throughout these experiments. The surface of these solutions had a diameter of 6 cm. The amount of growth at any particular time was judged by inspection, by estimating the diameter of the mat in centimeters. In recording these observations, the figure indicating the size of the growth was often qualified by such terms as "thin," "heavy," "wrinkled," and in comparing various cultures, such

¹ J. J. Willaman, *Botan. Gaz.*, 1920 (in press).

modifications were taken into consideration. Admittedly this method is not exact; but practice has given the writer what he considers is all the accuracy warranted by the eccentricities and irregularities of such culture studies. The determination of the dry weight of mycelium was impracticable in these studies for two reasons: first, because of the difficulty of freeing the mats of fungus from mother liquor without losing parts of the mycelium; and second, because not only the total growth but the rate of growth was wanted. Duplicate, and sometimes triplicate, sets were employed, only the average of which are here reported.

The amount of sporulation was likewise estimated by inspection, and recorded by indicating one or more + signs (see Table I). These signs indicate the *relative* and not the *absolute* amount of spore tissue, as compared with the amount of vegetative growth. Thus, if a 1.5 cm. mat was completely covered with spores, it was recorded 1.5; if a 5 cm. mat bore
++++

about 1.5 cm. of spore tissue, it was recorded 5, since the amount of sporu-
++

lation relative to vegetation is small. This method was adopted because reproduction is not an entirely separate phase, since a certain amount of vegetation is first necessary. Hence, vegetation can be considered as an absolute, while reproduction is only a relative, function.

The fungus was perpetuated in the laboratory on soaked dried peaches in deep petri dishes, autoclaved at 12 pounds pressure for 10 minutes. The growth was rapid, and gave an abundant supply of spores.

Preparation of Media.

The fruit juices were prepared by soaking the sound, commercial desiccated material in an excess of water for 24 hours, steaming at 100° for about 20 minutes, then draining and squeezing through cheese cloth. Sometimes the pulp was moistened and squeezed a second time. If the juice was for future use, it was placed in plugged Erlenmeyer flasks and sterilized at 100° for about 30 minutes.

The basal medium for all the vitamine tests consisted of Currie's mineral solution,¹ plus asparagine for a source of nitrogen, plus sucrose. Its composition was as follows: Water, 1000 cc.; monopotassium phosphate, 1.0 g.; magnesium sulfate (7H₂O), 0.25 g.; ferrous sulfate (7H₂O), 0.05 g.; 0.1 N sulfuric acid, 10 cc.; asparagine, 20 g.; sucrose, 80 g.

The chemicals were of the ordinary C. P. grade, the sucrose being "rock candy." Several other trial media indicated that calcium, sodium and chlorine added nothing to the value of the above medium. The 0.1 N sulfuric acid was added to give a certain acidity to the medium comparable to that of fruit juice. *Sclerotinia* will endure a rather wide range of reaction and still grow and reproduce normally. Indicator determina-

¹ J. N. Currie, *J. Biol. Chem.*, 31, 15 (1917).

Results showed that the cultures in these tests had P_H values between 3.8 and 4.3, which is well within the possible range of this organism. The phosphate and asparagine in the medium served as buffers.

The media were autoclaved at 12 pounds pressure for 10 minutes. This inverted about $\frac{1}{4}$ of the sucrose, and made the solution faintly yellow, but neither of these changes is detrimental to *Sclerotinia*. Some tests on the effect of high temperature on the vitamins and on fruit juices, given later, showed no detectable injuries.

Many compounds of nitrogen other than asparagine were tried, and will be indicated in their proper place. Ammonia and nitrate nitrogen can be utilized, but rather poorly; and peptone is too highly contaminated with vitamins to be of service in a basic medium.

IV. Experimental Data.

Preliminary.

In order to show the course of development of the fungus on various dilutions of fruit juices, the data in Table I are presented.

TABLE I.
The Course of Development of *Sclerotinia cinerea* on Various Fruit Juices

Medium			Age of the cultures in days												
Culture No	Cc Prune juice	Cc Water	3	4	5	6	7	8	9	10	11	12	13		
107	25	0	3 ⁺ +-	3.5 +	4 +	4 ++	4 ++	4.5 ++	5 +	5 +	5 +	5 +	5.5 +		
107a	20	5	3 +-	3.5 +	3.5 +	4 +	4 +	4 +	4.5 +-	4.5 +-	4.5 +-	4.5 +-	4.5 +-		
107b	15	10	2 -	3 +	3.5 +	3.5 +	3.5 +	3.5 +	3.5 +	3.5 +	3.5 +	3.5 +	3.5 +		
107c	10	15	1.5 -	2 -	2 -	2 -	2 -	2.5 -	2.5 -	2.5 -	2.5 -	2.5 -	2.5 -		
Peach juices															
108	25	0	3 -	3.5 +-	4 +	4.5 ++	5 ++	5 ++	5 +++	5.5 +++	5.5 +++	6 +++	6 +++		
108a	20	5	3 -	3 +-	3.5 ++	3.5 ++	4 ++	4 ++	4 ++	4 ++	4 ++	4 ++	4 ++		
108b	15	10	3 -	3.5 -	3.5 +-	4 ++	4 ++	4.5 +++	4.5 +++	4.5 +++	4.5 +++	4.5 +++	4.5 +++		
108c	10	15	2 -	2.5 -	3 +	3 +	3 ++	3 ++	3 ++	3 ++	3.5 +	3.5 +	4 +		
Apricot juices															
109	25	0	4 -	4 -	4.5 -	4.5 -	5 -	5.5 -	6 -	6 -	6 -	6 -	6 -		
109a	20	5	2 -	4 -	4 +++	4.5 +++	5 ++	5 ++	5 ++	5 ++	5 ++	5 ++	5 ++		
109b	15	10	3 -	3.5 -	3.5 +	4 +	4.5 -	4.5 -	5 -	5 -	5 -	5 -	5 -		
109c	10	15	2 -	3 -	3 -	3 +-	3.5 +-	3.5 -	4 -	4 -	4 -	4 -	4.5 -		

* See Section III for explanation of figures and signs. Complete growth is +++++.

It will be noted (1) that practically complete growth is accomplished within 10 days; (2) that sporulation begins about the third or fourth day; (3) that the amount of vegetation is not proportional to the concentration of the juice, the fungus being unable to utilize the greater amounts of nutrients in the same degree that it does the lesser; (4) that reproduction is more abundant on the peach juice than on the others; (5) that the higher concentrations are not necessarily the optimum for reproduction.

Since peach juice appeared to be the best adapted for the work at hand, it was used in most of the succeeding experiments.

TABLE II
Efficiency of Various Compounds of Nitrogen for *Sclerotinia*, Used in the Basal Medium of Salts and Sucrose

Culture No	Nitrogen compound and amount used in 25 cc. of medium G		Age of cultures in days		
			4	7	10
119	NH ₄ NO ₃	0.25	0.5	0.5	0.5
127	NH ₄ NO ₃	0.05	0.2	0.5	0.5
120	NH ₄ Cl	0.40	0.2	0.5	0.8
128	NH ₄ Cl	0.08	0.3	0.5	0.5
121	NaNO ₃	0.50	0.5	0.5	0.5
129	NaNO ₃	0.10	0.2	0.5	0.5
130	Egg white	0.10	1	3	6
			-	-	+++
123	Urea	0.20	Germinated, but no growth		
131	Urea	0.05	Germinated, but not growth		
124	Glycine	0.30	0.5	3	3.5
				++	++
132	Glycine	0.06	0.3	1.5	3
					++
141	Peptone (Witte)	0.50	3	4.5	6
			-	-	-
140	Peptone (Witte)	0.10	0.8	1.5	2
				-	-
142	Asparagine	0.10	0.5	1	1.5
				-	-

Table II presents the results of experiments designed to test the effectiveness of various sources of nitrogen used in conjunction with the mineral-sucrose basal medium. At the time these tests were made, the vitamine hypothesis for *Sclerotinia* had just been suggested to the writer. On this basis, the apparent great differences in availability of these nitrogen compounds could easily be explained by assuming a vitamine contamination in the successful ones, and the lack of it in the unsuccessful. McCollum¹ and Williams² found considerable vitamine B in commercial lactose, and the latter found it abundant in Witte's peptone, which examples show the possibilities of vitamine contamination in many substances.

To test this point, a series of cultures were made, using various prepara-

¹ E. V. McCollum and M. Davis, *J. Biol. Chem.*, 23, 181 (1915).

² R. J. Williams, *Ibid.*, 38, 465 (1919).

of vitamins, together with several compounds of nitrogen. The results can best be presented in the form of curves. Fig. 1 shows the effect of using glycine and prune juice, and asparagine and prune juice, singly and in combination. The growth curves show unmistakably that the nitrogen of asparagine, of glycine, or of 2 cc. of prune juice is insufficient

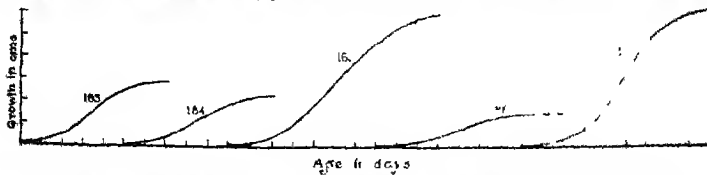


Fig. 1.—Availability of the nitrogen of glycine and of asparagine with and without the addition of prune juice.

183	25 cc. of basal medium + 2 cc. of prune juice	106.
184	" " " " 0.1 g. of glycine	
185	" " " " " " " + 2 cc. of prune juice.	
186	" " " " " " " asparagine.	
187	" " " " " " " + 2 cc. of prune juice.	

for normal growth; that the vitamins content of the 2 cc. of prune juice alone, together with its small quantity of contained nitrogen, is insufficient for good growth; but that the fungus can make excellent growth on either asparagine or glycine if the growth-promoting material of the 2 cc. of prune juice is also present.

In Fig. 2 are given the results of some tests with wort used in the commercial growing of baker's yeast and with a vitamins prepared from the

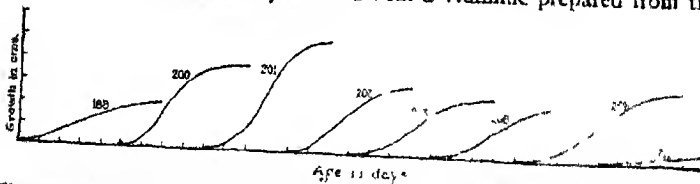


Fig. 2.—The presence of a growth-promoter in wort and in yeast vitamins, which enables *Sclerotinia* to utilize the nitrogen of $(\text{NH}_4)_2\text{HPO}_4$.

188	25 cc. of basal medium + 0.1 g. of $(\text{NH}_4)_2\text{HPO}_4$	
200	" " " " " " " + 1 cc. of wort.	
201	" " " " " " " 5 " " "	
202	" " " " " " " 1 cc. of wort.	
203	" " " " " " " 5 " " "	
208	" " " " " " " 0.1 g. of $(\text{NH}_4)_2\text{HPO}_4$ + 1 cc. of vitamins.	
209	" " " " " " " 5 " " "	
211	" " " " " " " 5 cc. of vitamins.	

wort by means of fullers' earth.¹ The growth curves indicate that diammonium hydrogen phosphate alone will not support growth; that the

¹ Both the wort and the vitamins were kindly furnished by Dr. R. J. Williams.

wort alone will support growth fairly well, but that the wort and the diammonium phosphate together constitute an excellent medium. Likewise, the vitamin preparation served to make the ammonia nitrogen more useful to the fungus, although the results are not striking. It should be remarked, however, that Cultures 208 and 209, containing the prepared vitamin, showed marked reproduction, a phase which will not be considered here.

Fig. 3 presents another series of cultures, using peptone. Lloyd's alkaloidal reagent, a variety of fullers' earth with a high adsorptive capacity towards alkaloids,¹ and also towards vitamine B,² was shaken with a solution of the peptone, in order to see whether it was a contained vitamine that gives this form of nitrogen its marked growth-promoting



Fig. 3 — The presence of a substance in peptone (Witte) and in alcoholic extract of wheat embryo that promotes the growth of *Sclerotinia*.

179	25 cc. of basal medium + 0.1 g of peptone	
180	" " " " " " " "	shaken with fuller's earth.
181	" " " " " " " "	" " " " " + alco-
	holic extract of wheat embryo	

properties with *Sclerotinia*. Also, a preparation of the alcoholic extract of wheat embryo was added to the "devitaminized" peptone. The growth curves show that apparently there is an accessory food factor in the peptone that can be at least partially removed by shaking with fullers' earth, and that the wheat embryo extract contains a similar substance that can enhance the nutritive value of the peptone.

Accommodation of *Sclerotinia* to Low Supplies of Vitamins.

In order to test the behavior of *Sclerotinia* over long periods of time on media low in vitamins, the series shown graphically in Fig. 4 was arranged. For comparison, the growth on a typical fruit juice medium is included. It will be seen that in most cases on any medium the growth is greatest during the first week and a half; that its growth during this period is roughly proportional to the supply of vitamins; that its growth following this period is very slow. Whether this long-continued slow

¹ J. U. Lloyd, *J. Am. Pharm. Assoc.*, 1916, Apr.-May. We wish to acknowledge our indebtedness to Prof. Lloyd for our supply of this material.

* A. Geldell, *U. S. Public Health Report*, 31, 364 (1916).

growth represents a struggle on the part of the fungus to distribute the previously absorbed vitamine throughout a greater bulk of tissue, or whether during this period the fungus is synthesizing its own vitamine, or whether it is doing without it altogether, is not known at present. In most cultures, after the initial period of relatively rapid growth has passed, there is scarcely any visible change for the next 10 or 15 days except a

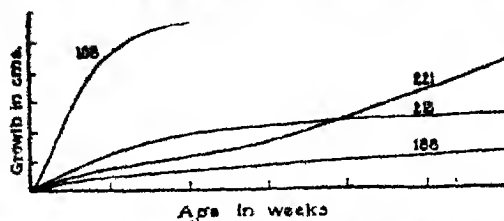


Fig. 4.—Growth of *Sclerotinia* over long periods of time on low levels of vitamine supply.

108 Peach juice medium (Table 1)

188 25 cc. of basal medium + 0.1 g of $(\text{NH}_4)_2\text{HPO}_4$. No source of vitamine added.

213 25 cc. of basal medium + 0.1 g of $(\text{NH}_4)_2\text{HPO}_4$ + 0.2 cc of peach juice.

221 25 cc. of basal medium + 0.07 g of asparagine. No source of vitamine added.

decided darkening of the mycelium. Then tufts of new, white mycelium begin to appear on the surface of the old. These slowly spread until in some cases they nearly cover the older portion. Although direct evidence is lacking, it is plausible that during this quiescent period autolytic changes are taking place in the oldest cells. This would liberate the contained vitamine into the medium or into the adjacent healthy cells, and a growth could recommence.

It is not known whether the better growth on asparagine than on diammonium hydrogen phosphate is due to a greater availability of the former or to the presence of contaminating vitamine. It should be pointed out here that in no case has the writer been sure that vitamins were entirely excluded from his cultures. As previously mentioned, in the method of inoculation used, several hundred spores are in most cases transplanted by the platinum wire in a single clump to the surface of the medium. In the case of yeast, as pointed out by Williams,¹ a single cell will show practically no division in a vitamine-free medium; whereas if many cells are present, the rate of division increases in proportion to their number. The writer has not had opportunity to make single spore inoculations. In the case of *Sclerotinia* the transfer must be made on the surface to secure normal growth, and attempts to do so with a single spore have so far been unsuccessful. It has often been observed, however, that single spores of this fungus in distilled water grow hyphae which

¹ R. J. Williams, *J. Biol. Chem.*, 38, 465 (1919).

are several hundred times the volume of the spore. How far it would develop in a nutrient medium complete except for lack of vitamine is a fact which should be ascertained.

In order to show that exhaustion of a medium and hence cessation of growth is often occasioned by the consumption of all the vitamine in the solution, the series of cultures shown in Fig. 5 was arranged. It is clear that in 223 and 224 growth ceased principally because the vitamine was consumed, and not because of an exhaustion of the nitrogen, minerals, or sugar; since when a new supply of vitamine was added the medium

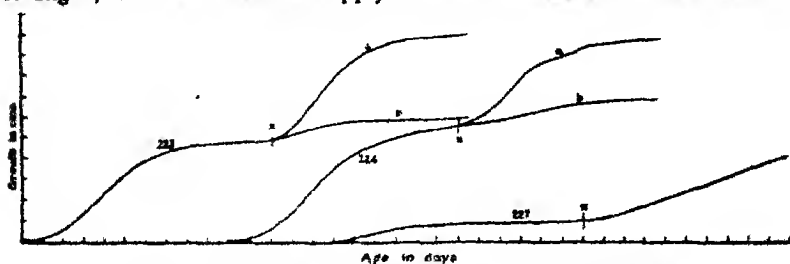


Fig. 5.—Exhaustion of the vitamine content of the medium.

223 25 cc. of basal medium + 0.07 g. of asparagine + 2 cc. of peach juice in each of 2 flasks. At x the fungus was removed from each flask; 4 cc. of vitamine preparation was added to a, and both were reinoculated.

224 is a repetition of 223.

227 25 cc. of basal medium + 0.07 g. of asparagine + 0.2 cc. of vitamine preparation. At x 4 cc. of vitamine was added, without removing the fungus.

could support another growth of the fungus. Number 227 brings out more vividly the reason for the failure of growth on a medium lacking in vitamine. This culture had made a growth of but one cm. in 11 days; the addition of some vitamine solution induced an immediate growth response. It is conceivable that the toxin explanation of failure of fungi to grow on "used" media, offered especially by Lutz,¹ in many cases is simply a case of exhaustion of a growth-promoting factor.

Preparation of Vitamines from Various Sources.

Since the evidence pointed to the fact that *Sclerotinia* requires a vitamine which occurs in several natural materials, which is rather heat stable, and which is adsorbed by fullers' earth, it was thought desirable to make vitamine preparations from a variety of sources, for the following reasons: (1) to obtain information concerning their possible identity with the water-soluble B; (2) to see whether a variety of sources would not furnish preparations which differed in their relative effect on growth and reproduction in *Sclerotinia*; (3) to gain some knowledge of the distribution and relative abundance of these substances in plant and animal materials; (4) and, in

¹ O. Lutz, *Ann. Mycol. von Sydow*, 7, 91 (1909).

a few instances, to obtain preliminary evidence concerning the possible role of vitamins in the phenomena of correlation in plants.

The method of obtaining the vitamins by means of Lloyd's alkaloidal reagent was used in all of these experiments. It adsorbs the vitamins from an acid solution, and releases them in an alkaline. This method was adopted because (1) it is characteristic of vitamin B, with which the writer, after a few preliminary trials, was convinced he was working; (2) it makes a more or less well defined separation of the principles studied from the other nutrients of the materials; (3) it tends to exclude the presence of toxic compounds, such as tannin, from the tests. The latter point is very important, since in one case a water extract of dried plum material inhibited the growth of the fungus entirely, while a very active vitamin preparation could be made from the material.

In the preliminary work with the juice of peaches and prunes, it was found that the presence of the pectin in the juice almost wholly inhibited the adsorptive property of the fullers' earth (see Table III, Numbers 222, 223, 227-230). When the pectin was precipitated with 2 volumes of 95% alcohol, and the alcoholic filtrate shaken with the earth, good adsorption was obtained. Williams and Seidell¹ found that acidified alcohol could be used to extract the vitamin from fullers' earth; since, however, they do not state the strength of acid or of alcohol used, it is not known whether their method and the writer's are really contradictory or not. It was decided to adopt this medium of about 65% alcohol for the preparation of the vitamins. It was slightly acid, by virtue of the natural acidity of most of the materials, and of the addition of a few drops of 1% sulfuric acid. It had certain other advantages over an aqueous medium, such as greater ease in filtration and the exclusion of starch and proteins in some of the materials.

Trials were conducted to ascertain the best conditions for the extraction, amount of Lloyd's reagent, time of shaking with it, effect of boiling the alcoholic solution with it, amount and kind of alkali to be used in liberating the adsorbed vitamin. For the last, Williams' method,² using saturated barium hydroxide solution, was adopted, since subsequent acidifying with sulfuric acid left no residual salt in the preparation. Table III gives the methods and results of these trials. The general procedure consisted in the precipitation and filtration of the pectin, the thorough mixing of the filtrate with the Lloyd's reagent in a mortar, shaking in a mechanical shaker for the specified length of time, filtering the fullers' earth through paper on a Büchner funnel, washing once with slightly acidified 65% alcohol, macerating the fullers' earth with the saturated barium hydroxide,

¹ R. R. Williams and A. Seidell, *J. Biol. Chem.*, 26, 431 (1916).

² R. J. Williams, *Ibid.*, 38, 465 (1919).

again shaking in the machine for 30 minutes, filtering through thin asbestos on a Büchner funnel, carefully neutralizing the filtrate to phenolphthalein with dil. sulfuric acid, then adding an excess of 5 to 10 drops of 0.1 *N* sulfuric acid to remove the barium completely and leave a faintly acid solution. This solution was now boiled for a time, in order to concentrate it and to bring the particles of barium sulfate into a filterable condition. After filtration the vitamin solution was brought to a volume corresponding to that of the original fruit juice used. The above practice of boiling for indefinite periods at atmospheric pressure was not detrimental to the vitamins. A great many trials by the writer, and the experience of almost all other workers with vitamin B, have shown that many hours of heating at 100°, either in alcohol or in water, provided the solution be acid, can be practiced with impunity.

In those cases where the treatment with fullers' earth was done in an aqueous solution of the fruit juice, the removal of the pectin was first accomplished as usual, then the alcohol removed from the filtrate by boiling. The residue was then made up to the original volume of the juice and treated with the earth.

An examination of the data in Table III reveals the following facts. (1) The first series shows that very little vitamin can be adsorbed in the presence of pectin. That the pectin itself can adsorb vitamin fairly well will be brought out later. (2) The second and third series show that boiling the alcoholic solution of vitamin with the Lloyd's reagent for 10 minutes is rather effective in removing the vitamin. Other trials, not presented here, showed, however, that this procedure is not quite so dependable as shaking at ordinary temperature, so it was abandoned. (3) Numbers 254 and 258 show that 2 hours of shaking are as effective as 5 hours in the adsorption of vitamin. (4) The third series makes a comparison concerning the amount of the fullers' earth required. Seidell¹ found that 5 g. per 100 cc. of autolyzed yeast removed practically all of the antineuritic factor. The data show that this is not the case with the materials used here. Nine g. removes appreciably more than does 4 g. Since it is very obvious that even 9 g. does not remove a very large proportion of the vitamin, 13 g. was used in all subsequent work. A larger amount was not feasible because the volume occupied by the fullers' earth and the amount of mother liquor occluded in it made comparative separations impossible. (5) Considerable variations in the amount of sporulation are noticeable in the table. This will be considered at some length in a later section.

From the above observations the following procedure was decided upon and rigidly adhered to in all the preparations of vitamin designed for

¹ A. Seidell, *U. S. Public Health Report*, 31, 364 (1916).

TABLE III.
Efficiency of Various Methods of Preparing the Vitamine by Means of Lloyd's Reagent.

Culture No.	Material	Kind of solution used with 100 cc. of reagent.	Amt. of reagent per 100 cc. of solution, G.	Time of shaking, Hrs.	Activity of the various amounts of vitamin-containing solutions in 25 cc. of medium.														
					0 cc.			0.3 cc.			1 cc.			2 cc.			3 cc.		
					4 days	7 days	10 days	4 days	7 days	10 days	4 days	7 days	10 days	4 days	7 days	10 days	4 days	7 days	10 days
222	Peach juice, vitamin not removed	0.3	0.6	0.8	0.8	2.5	2.5	2	4.5	5.5
227	Vitamin from 222	Aqueous, pectin present	7	10	0.3	0.6	0.8	0.3	0.5	0.8	1	1	1	2	3.5	4
224	Residue from 227	0.3	0.6	0.8	1.5	4	6
248	Peach juice, vitamin not removed	0.3	0.5	0.7	1	2.5	4	0.5	3	4
250	Peach juice, same as 248, after removal of pectins	0.3	0.5	0.7	0.5	2.5	4	1	4	5
254	Vitamin from 250	Alcoholic	7	2	0.3	0.5	0.7	1	3	4	3	4	5.5
																	+++	++++	++++

252	Residue from 254	0.3	0.5	0.7	0.3	1.5	3	1	4.5	6
258	Vitamine from 250	Alcoholic	7	5	0.3	0.5	0.7	2	4	4.5	...	+	4	6
256	Residue from 258	0.3	0.5	0.7	0.5	2.5	3	...	1	3.5	6
268	Vitamine from 250	Alcoholic	7	Bolled 10 min.	0.3	0.5	0.7	1	3	3.5	...	2	4	5.5
266	Residue from 268	0.3	0.5	0.7	0.5	1	2	...	1	2.5	5
300	Peach juice, pectin removed	0.2	0.4	1	2	5	3.5	...
296	Vitamine from 300	Alcoholic	4	Bolled 10 min.	0.2	0.4	1	1	2	2.5	...
297	Vitamine from 300	Alcoholic	9	Bolled 10 min.	0.2	0.4	1	1	2.5	3.5	...
298	Vitamine from 300	Alcoholic	4	Shaken 2 hrs.	0.2	0.4	1	0.8	1	2.5
299	Vitamine from 300	Alcoholic	9	Shaken 2 hrs.	0.2	0.4	1	1	3.5	5.5

TABLE IV.
Relative Activity of Vitamine Preparations from Various Sources.

Culture No.	Number and source of the vitamin preparation	Activity of the various amounts of the preparations in 25 cc of medium														
		0 cc.			0.3 cc.			1.0 cc.			2.0 cc.					
		4 days	7 days	10 days	4 days	7 days	10 days	4 days	7 days	10 days	4 days	7 days	10 days			
	Standard peach decoction (control)	0	3	0	8	1	2	2	5	1	3	4	1	5	4	6
313	306 Peach decoction					0.3	1	3	2	1	2	2.5	1.5	2.5	2.5	++
370	334 Plum decoction					1	2	2		2.5	3.5	6	3	5	6	+++
326	246 Mycelium of <i>Sclerotinia</i>								1.5	0.3	1.5	2.5	1	1	1	1.5
330	247 Mycelium of <i>Sclerotinia</i>							1	1	1	1.5	2	0.8	2.5	3	-
373	346 Mycelium of <i>Sclerotinia</i>					0.3	1	1	1	0.5	1.5	2	2	4	4	-
530	496 Mycelium of <i>Aspergillus</i>							0.8			1.5			2.5	...	++
533	506 Sphorophore of <i>Sclerotinia</i>							1			1.5			4.5
376	362 Sphorophore of <i>Collybia</i>					1.5	2.5	3		2	3.5	3.5	2	3	3	3
476	446a Baker's yeast, autolyzed					1.5	3	4		2.5	3.5	4.5	2.5	5	5.5	+++

322	321	Pollen of maize	0.3	0.8	2	2	3.5	3.5	2	3	3.5
								-	++	+	+	+++	+++	+++
485	475	Bean sprouts	2	2.5	3	2	3	4.5	2.5	4	5.5
						+	-	-	+	+	-	+	+	+
382	365	Sprouts of potato tubers	1	2	2.5	1	2.5	2.5	2	3	3
						-	+-	+-	+-	+	+	+	+	+
466	364a	Wheat kernels	0.6	2.5	3.5	1	1.5	1.5	1.5	2	2.5
							-	-	-	-	-	-	-	-
379	364b	Wheat kernels, sprouted	2.5	3.5	4	2	3.5	3.5	1	1.5	2
						-	-	-	-	-	-	-	-	-
443	364c	Wheat kernels sprouted	1.5	2	2.5	...	1	1.5	1	1.5	2
						-	-	-	...	-	-	+	+	+-
385	365a	Terminal buds of bean plant	2	3	3.5
									+++	+++	+++			
386	366b	Lateral buds of bean plant	2	3	3
									+	++	++			
387	367	Young tomato leaves	1	3	3.5
									+	-	-			
394	390	Rice polish	0.3	0.8	1.5	0.5	1	2	1	2.5	2.5
								-		-	-	+	+	+
437	415	Skim milk	0.7	1.5	1.5	0.8	1.5	2	1	2	2.5
							-	-		-	-	+-	+-	+-
469	447	Paucireatin	1	2.5	3	1.5	2.5	3	1.5	2.5	3.5
						-	-	-	+	+-	+-	-	+-	-

purposes of comparison. All quantities of materials were based on the dry matter content in grams of the sample in hand. Thus:

dry matter $\times 30$ = volume of 65% alcoholic extract of the material,

dry matter $\times 4$ = grams of Lloyd's reagent used,

dry matter $\times 32$ = volume of saturated barium hydroxide solution used to extract the vitamine from the earth,

dry matter $\times 10$ = volume of the final vitamine preparation.

In the case of a succulent material, *e. g.*, potato sprouts, a certain water content was assumed, sufficient 95% alcohol added to it to bring the resultant extract to 65%. the mixture ground with sand, enough 65% alcohol added to bring the total to the volume required by the above formula, the whole boiled for a few minutes, then filtered through paper, and washed once with a few cc. of 65% alcohol. The filtrate was then used in the manner described above, shaking with the fullers' earth for 2 hours. The final vitamine preparations were placed in bottles or test-tubes, stoppered with cotton, and sterilized at 100° for about 15 minutes.

Table IV presents the results of culture tests with the various vitamine preparations, roughly grouped according to the character of the material. Following is a description of the materials used, and a brief discussion of the results:

306. Dried apricots, soaked, steamed, and the juice expressed. This fruit, like all others of *Prunus* and *Malus*, is a natural host of *Sclerotinia*, and is a source of abundant vitamine supply. Sporulation is usually prominent in media containing vitamins from these sources.

334. Ripe plum. The material was collected in the summer of 1918, dried in an oven at 85-95°, ground to a powder, and stored in a bottle. After this rather vigorous treatment it still yields a very active vitamine preparation, at least for vegetative development.

246. Four mycelial mats of *Sclerotinia* that had grown on diluted peach juice.

247. Six mycelial mats of *Sclerotinia* grown on a synthetic medium plus vitamine. Both this and the preceding show moderate amounts of vitamine for vegetative purposes.

346. The fungus mats from Numbers 252, 256 and 258, Table III. Although these cultures had shown good sporulation, the vitamine preparation from them shows only vegetative activity. This phase will be discussed later.

496. Four mycelial mats of *Aspergillus niger*, grown on a synthetic medium free from added vitamine. This fungus grows vigorously, without any known source of vitamine, on the most highly purified of synthetic media, as Currie reports.¹ Currie, in correspondence with the writer, states that an extract of old mycelium or of vigorously sporulating tissue of *A. niger* strongly accelerates the growth of this fungus. The power of accommodation to low supplies of vitamine will be discussed later.

506. Sporophore of *Scleroderma* sp., one of the common puff balls. The tissue was beginning to ripen. This is another material high in sporogenous tissue.

362. Sporophore of *Collybia* sp. This was selected to obtain another preparation from a spore tissue. It is high in the reproductive factor.

446a. Baker's yeast, autolyzed 48 hours. This is the standard source of strong preparations of vitamine B. The present preparation is seen to be very active in promoting both growth and reproduction in *Sclerotinia*.

¹ J. N. Currie, *J. Biol. Chem.*, 32, 15 (1917).

321. Pollen of maize, *Zea mays*. This was used in order to have a preparation from the spores of another plant. It is seen to be very active in producing reproduction in *Sclerotinia*; in fact, this is one of the most active preparations the writer has found.

475. Bean sprouts, species unknown, but it is the material used in "bean-sprout chop suey." The material was obtained from a Chinese shop in Chicago. According to Chick and Hume¹ the sprouting increases the vitamins in legumes in particular. Considerable vitamin is demonstrated in the present preparations.

365. Sprouts of potato tubers, *Solanum tuberosum*. The sprouts were about one cm. long.

364. Kernels of wheat, *Triticum sp.* 364a, dry kernels, before sprouting or soaking; 364b, sprouted 4 days in light, sprouts 2 cm. long; 364c, 8 days, sprouts (leaves) 8 cm. long. This series was designed to show whether any increase in vitamins could be demonstrated during sprouting, as has been claimed by Chick and Hume¹ for vitamin B, and by Chick and Hume and by Greig² for the antiscorbutic factor. In all 3 the kernel, roots and sprouts were included in the preparation. The tests with *Sclerotinia* were very irregular; so much so that the presence of some toxic material is indicated in the higher additions of vitamin. The only significance attached to these data is that they do demonstrate the existence of the vitamin, at least for vegetative purposes, in the wheat both before and after sprouting. There is some indication that reproduction is increased by the preparations from the older sprouts.

366. Scarlet runner bean, *Phaseolus multiflorus*. This plant is the classic example of correlation influences in plants. The lateral stem buds do not grow as long as the terminal bud is present and growing; if the latter is removed, the next lowest lateral bud begins to develop and becomes the growing point of the plant. It was suggested by Dr. William Crocker, of the University of Chicago, that the influence of vitamins might be concerned in these active and dormant buds. Number 366a is a preparation from terminal buds, 366b from lateral buds. Both preparations are seen to carry the vitamins in about equal amount. It is not felt that this test proves or disproves the possible controlling effect of vitamins in this plant, since only very small amounts of material were available, and since the technique of such tests with *Sclerotinia* is not as yet capable of showing positively small differences between preparations. However, the presence of vitamin in both kinds of buds is unmistakably demonstrated, with the terminal buds possibly promoting more reproduction than the lateral.

367. Young actively growing leaves of tomato, *Lycopersicon esculentum*. The positive results with this preparation are in line with the findings in animal feeding experiments that the green leaves of plants are plentifully supplied with both vitamin A and vitamin B.

390. Rice polish. This is the long-known source of vitamin B, the lack of which causes beri-beri, or polyneuritis. This preparation is only moderately active in promoting growth in *Sclerotinia*.

415. Skim milk. This is known to contain the water-soluble B in fairly high amounts, and a preparation of "protein-free milk"³ is much used in animal feeding for this purpose. The present preparation is only moderately active towards *Sclerotinia*.

447. Pancreatin (Parke, Davis Co.). Eddy⁴ has shown that pancreatic extracts contain considerable amounts of vitamin B. It is also demonstrated in the present preparation.

¹ H. Chick and E. M. Hume, *J. Roy. Army Corps*, 29, 121 (1917).

² E. D. W. Greig, *Indian J. Med.*, 4, 818 (1917).

³ T. B. Osborne and L. B. Mendel, *Carnegie Inst. Pub.*, 156, Pts. I and II (1912), Washington.

⁴ W. H. Eddy, *J. Biol. Chem.*, 27, 113 (1916).

The Number of Vitamines Involved and their Identity.

Several very important considerations should be pointed out in connection with the preceding experiments on vitamine preparations from different sources: (1) Every material examined, both plant and animal, supplies a vitamine active towards *Sclerotinia*. (2) Although all the vitamine preparations induce growth, only a relatively few induce reproduction. (3) The amount of reproduction in any given case is not necessarily proportional to the amount of vegetation. (4) The amount of growth is not proportional to the amount of vitamine preparation added. In fact, in some cases the higher additions promote less growth than the lower. Whether this is due to some toxic material extracted either from the material or from the fullers' earth is not known. (5) The cultures showing the greatest amount of reproduction are 322, from pollen, 376, from fungous sporophore; 385, terminal buds of *Phaseolus*; 476, yeast; 530, sporulating mycelium of *Aspergillus*; 533, sporophore of *Sclerotinia*; 254 and 258, peach juice (Table III); and several of the peach juice media in Table I. It is noteworthy that most of these materials are characterized by high metabolic activity, either actual or potential. The fruit juices are not so characterized, but, on the other hand, they are the natural medium for this fungus. There is apparently some relation between the potential growth energy of a tissue and its value as a source of vitamine for the production of tissue in *Sclerotinia* with similar potential growth energy.

The above observations indicated the possible existence of two vitamine factors, one for vegetative growth and one for reproduction. There is a voluminous literature dealing with the question of vegetation vs. reproduction in plants. Among the factors so far discovered that control or affect this ratio are light, temperature humidity, oxygen, age of the plants, supply of nutrients, and the ratio of certain nutrients, especially of the carbon and nitrogen. The latter factor is apparently very important for many seed plants, but has not been demonstrated to be of so much significance in the fungi. Among the latter plants light,¹ the supply of nutrients,² sudden reduction in the supply of nutrients³ and the dependence on a particular plant decoction,⁴ are of importance in affecting reproduction in certain species. In the case of *Sclerotinia* these factors do not appear to operate in determining the relative proportion of the vegetative and reproductive phases, as was discussed in Section III. The controlling influences seem to be the substances of the nature of vitamins. So far as the writer is aware, no one has suggested this before for any species of

¹ G. H. Coons, *J. Agr. Res.*, 5, 713 (1916).

² V. I. Palladin, "Plant Physiology," trans. by Livingston (1918), Philadelphia (p. 294-299).

³ A. J. Pieters, *Am. J. Botany*, 2, 329 (1915).

⁴ G. F. Clinton, *Agr. Exp. Sta., Conn., Rpt.*, 1909-10, p. 733.

plant. Therefore, experiments were instituted to obtain information concerning this obscure phase of plant metabolism. Some of the specific problems involved are (1) the properties of the vitamine or vitamins; (2) the possible means of separating them from the materials containing them and from each other; (3) their relation to the already known vitamins; (4) their relation to the other nutritive materials of the medium.

As regards the chemical and physical properties of the vitamins in general, they have no common characteristics as a class. It is probable that water-soluble B contains nitrogen, since all preparations of it have contained nitrogen, and since Williams¹ has secured some evidence that it is an isomer of adenine. The occurrence of nitrogen in the other vitamins has not been investigated in any precise way. Fat-soluble A is destroyed by aeration at 100°;² the antiscorbutic C is destroyed by even lower temperatures;³ vitamine B resists autoclaving for at least an hour,⁴ 18 hours of boiling in benzene and in acetone,⁵ and 24 hours of hydrolysis in 20% sulfuric acid,⁶ Davis'⁷ vitamine, for the influenza bacillus, withstands 100° for 1 to 2 hours; Miss Lloyd's⁸ meningococcus vitamine withstands 120° for 45 minutes, and Shearer's⁹ is not destroyed by conc. hydrochloric acid at 100° for 6 hours. Drying is fatal to the antiscorbutic C,⁸ but not to the others, so far as tested. Vitamine B is adsorbed by fullers' earth,¹⁰ and to a certain extent by animal charcoal¹¹ and by dialyzed iron;¹² vitamine C is not adsorbed by either or by a Berkefeld filter;¹³ the meningococcus vitamine is adsorbed by filter paper.⁸ Vitamine B is precipitated by phosphotungstic acid,¹³ as are Bottomley's auximones.¹⁴ All the vitamins so far tested are soluble in water and in aqueous alcohol, with the possible exception of fat-soluble A. All preparations of vitamine B, as well as the peat auximones,¹⁵ give positive reactions with the Folin-Dennis color reagent for purines.¹⁶

¹ R. R. Williams, *J. Biol. Chem.*, 25, 437 (1916), R. R. Williams and A. Seidell, *J. Biol. Chem.*, 26, 431 (1916).

² H. Steenbock, P. W. Boutwell and H. E. Kent, *J. Biol. Chem.*, 35, 517 (1918).

³ A. F. Hess and L. J. Unger, *ibid.*, 35, 487 (1918).

⁴ E. V. McCollum and M. Davis, *ibid.*, 23, 247 (1915).

⁵ E. V. McCollum, *J. Am. Med. Assoc.*, 68, 1379 (1917).

⁶ E. A. Cooper and C. Funk, *Lancet*, 2, 1266 (1911).

⁷ D. J. Davis, *J. Infec. Dis.*, 23, 248 (1918).

⁸ D. Lloyd, *J. Path. Bact.*, 21, 113 (1916).

⁹ C. Shearer, *Lancet*, 1917, 59.

¹⁰ A. Seidell, *U. S. Public Health Report*, 31, 364 (1916).

¹¹ E. A. Cooper, *Biochem. J.*, 7, 368 (1913).

¹² A. Harden and S. S. Zilva, *Biochem. J.*, 12, 93 (1918).

¹³ R. R. Williams, *J. Biol. Chem.*, 25, 437 (1916).

¹⁴ W. B. Bottomley, *Proc. Roy. Soc. (London)*, 88B, 237 (1914); O. Rosenheim, *Biochem. J.*, 12, 7 (1917).

¹⁵ O. Rosenheim, *ibid.*, *J.*, 11, 7 (1917).

¹⁶ O. Folin and W. Dennis, *J. Biol. Chem.*, 12, 239 (1912).

Thus, in the present state of our knowledge of the vitamins, we must recognize them by what they do and not by their constitution or physical and chemical properties. But since there is such a great variation in the properties of the vitamins as a class, there was hope that various treatments of the *Sclerotinia* vitamins would yield useful information.

Adsorption in Alcohol and in Water.—Although, for the reasons given previously, the writer used an alcoholic medium for the adsorption by Lloyd's reagent of the vitamins listed in Table IV, others have used a water medium for isolating vitamin B. A series of separations was made from both media for comparative studies, by making an alcoholic (65%)

TABLE V.
65% Alcoholic Compared to Aqueous Media for the Adsorption of Vitamins by Fullers' Earth.

Culture No.	Materials and treatment.	Growth at 10 days with various additions of vitamins to basal nutrient medium		
		0.3 cc	2 cc.	5 cc
448	Vitamins prepared from fullers' earth in 65% alcoholic solution of peach juice.....	3.5	5	4 +++
451	Residue from 448.....	3.5	5	5
454	Vitamins prepared from fullers' earth in aqueous residue from 448.....	4	5	5
457	Residue from 454.....	3.5	6	6 ++
476	Vitamins prepared from fullers' earth in alcoholic solution of autolyzed yeast.....	4 +-	5 +++	6 ++++
479	Vitamins prepared from fullers' earth in aqueous residue from 476.....	2.5	3.5	3 +-
482	Residue from 479.....	3	3.5	3
497	Autolyzed yeast.....	4 +++	5 +++++	6 +++++
500	Vitamins prepared from fullers' earth in aqueous solution of 497.....	2.5	3.5	4.5 +
503	Residue from 500.....	4 +-	5.5 ++	6 ++++
485	Vitamins prepared from fullers' earth in alcoholic extract of bean sprouts.....	3.5	5.5	6 +
489	Vitamins prepared from fullers' earth in aqueous residue from 485.....	2	3	3.5 +-
492	Residue from 489.....	2	2.5	3.5

extract of the vitamine-containing material, shaking with fullers' earth, then freeing the filtrate from alcohol by boiling, and using fullers' earth again on the aqueous residue; or the fullers' earth was used directly on the aqueous extract of the original. Table V presents the results of the tests.

It will be noticed in the first series that the reproductive factor is present only in the vitamine removed in an alcoholic medium, and in the residue left after all the treatments. In the second series practically all the reproductive factor is removed in the alcoholic medium, very little being in the aqueous separation or in the final residue. In the third series, the original autolyzed yeast is very rich in this factor; an aqueous treatment with Lloyd's reagent removed but a small amount; and the residue from the latter was still rich in it, showing that the failure of the aqueous treatment was not due to a lack of the vitamine. In the fourth series, the reproductive factor did not appear in any fraction in appreciable amounts, showing that there is nothing inherent in the alcoholic treatment to bring out this factor where it does not already exist.

Reference to Table III brings out the fact that in most of the trials given there, the cultures containing vitamine preparations show far more reproduction than those containing additions of the fruit juices themselves. All of these separations were made in a 65% alcoholic medium.

The above tests suggest the existence of two vitamins, one of which is adsorbed by fullers' earth more readily in alcohol, the other more readily in water.

Adsorption by Gels.—The writer had occasion to prepare two samples of pectin from peach and prune juice. When tried on nutrient media, both preparations gave indications of rather strong adsorption of vitamine, although each had been dissolved in water and reprecipitated by alcohol 3 times. Again, it has been found that Witte's peptone is heavily contaminated by vitamine. Attempts to remove it with Lloyd's reagent in either alcoholic or aqueous extract have failed. Coagulated egg white also brings down considerable vitamine with it. No differentiating action, however, towards the two vitamins by the gels has been noticed.

Resistance to Heat.—The marked resistance of the *Sclerotinia* vitamine to boiling water and to boiling alcohol has been noted. In order to make a more careful determination of this, a sample of vitamine was prepared from prune juice without subjecting it to a temperature above 65° at any stage of the process. The prunes were soaked in cool water, macerated, the juice squeezed out without heating, the pectins precipitated, Lloyd's reagent used in the alcoholic filtrate, the vitamine preparation freed from barium sulfate by centrifuging, and then concentrated *in vacuo* at 65°. This was then used for the temperature tests. The required amount of this vitamine for each culture was placed in a plugged test-tube and autoclaved for the indicated period at 12 pounds pressure. Flasks con-

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aining the basal medium were sterilized separately, and then the autoclaved vitamins added to them. Table VI gives the data.

TABLE VI.
Effect of High Temperatures on the Vitamins of Prune Juice.

Culture No.	Duration of autoclaving at 12 lbs pressure Min.	Growth at 10 days with various additions of vitamins to basal nutrient medium.	
		0.5 cc	2 cc.
354	10	2.5	4.5
		—	—
355	20	3.5	4.5
		—	—
356	30	1.5	2.5
		—	++
357	40	3	3.5
		—	+
358	50	1.5	4
		—	—
359	60	1.5	2.5
		—	++
360	70	1.5	2.5
		—	+
361	80	2	3.5
		—	—

There is considerable immunity to the long-continued heating, although the cultures at the lower end of the series show somewhat less growth. There are also some slight indications that the reproductive factor is more abundant or active in the more strongly heated cultures.

The effect of prolonged heating on the nutritive value of a peach was tried by autoclaving a soaked peach for one hour at 12 pounds pressure. On inoculation, the fungus grew fairly well, and sporulated to a certain extent; but neither function was normal on this material. Such a test is hardly comparable to the tests on the isolated vitamins, however, because the high temperature decomposes the sugars with the formation of aldehydes, which are no doubt harmful to the fungus, and because most investigations have shown that the vitamins are less subject to injury while in the natural state than after isolation and purification.

Dialysis.—Dialysis through collodion was next tried. As a preliminary, 25 cc. of peach juice was dialyzed against running tap water for varying lengths of time. Table VII presents the results. The added vitamins represent equivalent amounts of the undialyzed original in each case.

The pectin of the juice evidently interferes with the dialysis through collodion, since there was still considerable vitamin left in Number 225 after 40 hours against distilled water. When the separated vitamin, however, is dialyzed, as in the second series, it all passes out of the dialyzing

bag during the first hour. This method apparently offers no means of differentiating between the two vitamins.

TABLE VII.
Rate of Dialysis of the Vitamins through Colloidion Treatment.

Culture No.	Material	Duration of dialyzing hours	Growth at 10 days with various additions of vitamins to basal nutrient medium	
			3 cc	12 cc
225	Peach juice	40	3 —	5 +—
221	Control, no vitamin added		0.8 0.3 cc	... 2 cc.
348	Vitamin	Not dialyzed	2 —	3 +—
349	Vitamin	1	1 —	2.5 —
350	Vitamin	3	0.8	1
351	Vitamin	6	0.8	0.5
352	Vitamin	9	1	0.8

Effect of Drying.—During the summer of 1918 the writer collected a series of samples of plum fruits for proximate chemical analysis. Portions of each sample were pitted and then dried in an oven at 85–95° for 24 to 48 hours, no particular precautions as regards temperature and time being considered necessary for the purpose in mind. The material was brittle, and could easily be ground to a fine powder. These samples yielded a very active growth-promoting vitamin, as witnessed by Number 370, Table IV. Whether the apparent lack of the unproductive factor in this sample is common to the whole series has not been determined as yet.

Folin-Dennis Color Reagent.—The vitamin preparations listed in Table IV were tested with the Folin-Dennis phosphotungstic acid reagent for purines.¹ One cc. of the preparation, 1 cc. of the reagent, 2 cc. of saturated sodium carbonate solution, and 6 cc. of water were used in each case, so that a rough indication of the comparative intensities of the reaction could be obtained. Positive reactions were given by all preparations, Number 447, from pancreatin, was very weak, while Numbers 321, 362, 390 and 415 gave the strongest test. Reference to Table IV shows that of these 4, the first 2, from pollen and fungous sporophore, are very active towards *Sclerotinia* both for vegetation and for reproduction; while the latter two, from rice polish and from milk, are not very active towards *Sclerotinia*, but are conventional sources of vitamin B in animal feeding experiments. Although there is a possibility of these results indicating a lack of identity between the *Sclerotinia* vitamin and the water-soluble B, too great weight cannot be attached to them, since with the method employed the color test is not quantitative, and since the number of examples of the above correlation are too few.

¹ O. Folin and W. Dennis, *J. Biol. Chem.*, 12, 239 (1912).

Comparative Value to *Sclerotinia* and to *Saccharomyces*.—In order to determine whether a preparation active towards the brown-rot fungus is also active towards yeast, and in the same proportion, 4 preparations were tested out by Mr. R. J. Williams, using his method of judging the content of water-soluble B in a solution by its ability to promote multiplication in yeast.¹ Table VIII presents the results. The data for the *Sclerotinia* growths represent equivalent amounts of the preparations, and hence are comparable among themselves. The same is true for the yeast. The comparison we wish to make is that these preparations which are the more active for vegetative growth in *Sclerotinia*, Numbers 106 and 334, are the weaker towards yeast; and the two which are the more active for reproduction in *Sclerotinia*, Numbers 321 and 362, are also the more active towards yeast.

TABLE VIII.
Comparative Value of the Vitamine Preparations to *Sclerotinia* and to Yeast.

Material.	Multiplication of single yeast cell in 18 hours	Growth of <i>Sclero- tinea</i> at 10 days Cm
Prune juice 106 (Fig. 1).....	30	5.5 —
Vitamine 334, plum (Table IV).....	13	6 —
Vitamine 321, pollen (Table IV).....	60	3.5 +++
Vitamine 362, fungus sporophore (Table IV)...	300	3 ++++

Relative Proportion of Vitamines to Other Nutrients.

Since many plants have been shown to have their vegetative and reproductive phases more or less affected by the proportions of the elements in the nutrient medium, it was thought desirable to ascertain whether the activities of *Sclerotinia* vitamines would be modified by various proportions of the nutrient elements. A high carbohydrate to nitrogen ratio usually favors early reproduction, with scant vegetation, while a low ratio leads to vigorous vegetation and scant or delayed reproduction.

The triangle method of Schreiner and Skinner² for operating 3 variables against each other was used in arranging the cultures. The 3 variables chosen were the sugar, nitrogen, and vitamine contents of the medium. The sugar was furnished by sucrose alone in those cultures given prepared vitamines, and by sucrose and the sugars contained in the fruit juice when the latter was used for vitamine. The nitrogen was furnished mostly by asparagine, but partly by the contained nitrogen in the juice and in the vitamine preparation. In each case an analysis of the juice for sugar and for nitrogen, and of the vitamine preparations for nitrogen was made and the calculated sucrose and asparagine added to bring th

¹ R. J. Williams, *J. Biol. Chem.*, 38, 463 (1919).

² O. Schreiner and J. Skinner, *Botan. Ges.*, 30, 1 (1910).

totals to the desired figure. Fig. 6 indicates the constitution of the cultures in the various regions of the triangle. Many series of this kind of culture were run; some covered all the points of the triangle, others only

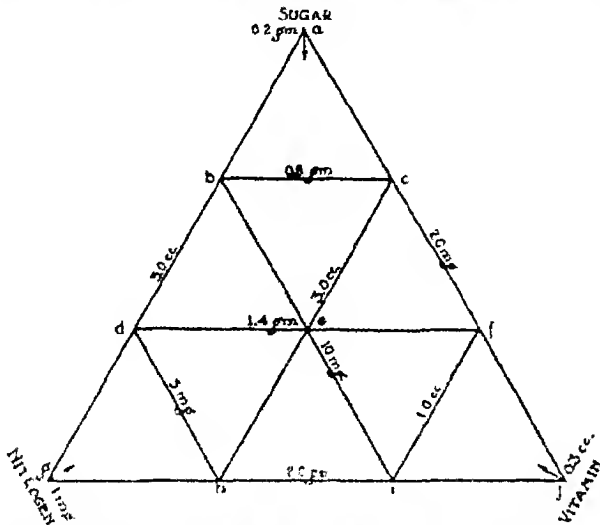


Fig. 6.—Diagram of nutrient media used to show the effect of varying the sugar, nitrogen, and vitamin contents.

certain areas. Instead of presenting all the data thus collected, Figs. 7 and 8 were constructed, representing a composite of all the cultures observed. The diagrams thus represent more or less ideal sets of cultures, although all the points on them have been verified several times. Fig. 7 represents the behavior of cultures which are supplied only with the vegetative vitamin factor; that is to say, so far as previous tests had shown, the preparations used did not show any indication of containing an appreciable amount of the reproductive factor. Fig. 8 represents the behavior of cultures supplied with preparations that had promoted both growth and reproduction in previous tests.

Considering Fig. 7 alone, first, the facts are brought out (1) that a moderate supply of all 3 factors, that is, near the center of the triangle, brings about maximum growth; (2) that vegetative growth is dependent more on the energy (sugar) supply than on the nitrogen, since point *g*, with the minimum of nitrogen, shows a larger growth than point *a*, with the minimum of sugar, and since the area of maximum growth is eccentric, lying towards the region of low nitrogen; (3) that the vitamin factor is intermediate in its influence, since vegetation is greater in area *f*, *i*, *j* than area *a*, *b*, *c*, but less than in area *d*, *g*, *h*.

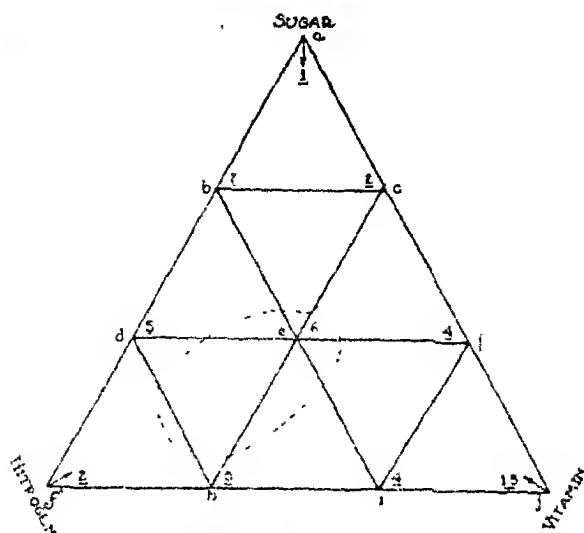


Fig. 7.—The growth of *Sclerotinia* on the media indicated in Fig. 6, when the added vitamins will promote only vegetation. The dotted line encloses the area of greatest vegetation.

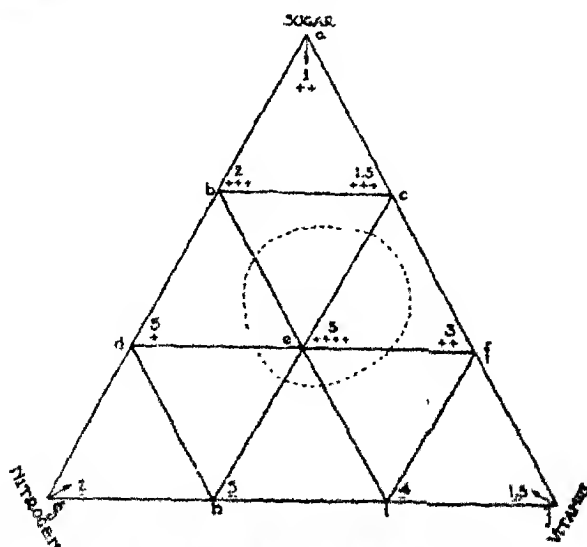


Fig. 8.—The growth of *Sclerotinia* on the media indicated in Fig. 6, when the added vitamins will promote both vegetation and reproduction. The dotted line encloses the area of greatest reproduction.

In Fig. 8, where the cultures show both vegetation and reproduction we see (1) that a moderate supply of all the factors—energy, nitrogen, and vitamine—brings both maximum vegetation and maximum reproduction near the center of the diagram; (2) that the more highly sporulating cultures lay toward the areas of higher vitamine, higher nitrogen, and hence lower sugar, the actual area of greatest reproduction being eccentric, as was the area of greatest vegetation in Fig. 7, but lying opposite to the latter; (3) that hence reproduction is more dependent on nitrogen than on sugar, whereas for vegetation the reverse is true; (4) that the same relations concerning vegetation hold as in Fig. 7, except that the points *c*, *e* and *f* show a little smaller vegetation, due to the energy demand of reproduction. These points fall in the area of lesser sugar supply; points

TABLE IX.

Effect of Varying the Nitrogen and Phosphorus Contents of the Medium on the Activities of the Vitamines.

25 Cc. of Basal Medium* used in Each Experiment.

Culture No.	Constitution of media			Growth at 8 days with various additions of vitamine.	
	Asparagine G	Vitamine No	Salt added.	0.3 cc.	2 cc.
508	0.05	334		2.5	5.5
510	0.02	334		3	5.5
512	0.05	334	0.07 ^g KH_2PO_4	3	5
514	0.05	362		2	3.5
516	0.02	362		3	3
518	0.05	362	0.07 g. KH_2PO_4	2.5	4
520	0.05	321		2.5	4
522	0.02	321		2.5	4.5
524	0.05	321	0.07 g. KH_2PO_4	5.5	5.5
526	0.05	0.3 cc. 334 + 0.3 cc. 321			2
527	0.05	2.0 cc. 334 + 2.0 cc. 321			4
528	0.05	2.0 cc. 334 + 0.3 cc. 321			5
529	0.05	0.3 cc. 334 + 2.0 cc. 321			4.5

* The basal medium contained salts (including phosphate) and sugar, but no nitrogen. The indicated additions of asparagine, therefore, constitute the sole source of nitrogen; but the indicated additions of KH_2PO_4 are in addition to that already present, which is 0.05 g. per culture.

v and *d* do also, but here the greater vitamine supply promotes greater utilization of the sugar.

Still further evidence was obtained that exaggerations in the proportions of nutrients can bring about only a quantitative and not a qualitative difference in the relative amount of vegetation and reproduction in *Sclerotinia*. Three preparations of vitamine were selected that showed very pronounced tendencies in the direction of their activities. Numbers 321 and 362 were very active in promoting reproduction, and Number 334 had showed good growth-promoting powers, but no power for reproduction. The attempt was made to reverse these activities by suitable proportions of nitrogen, phosphorus, and sugar in the medium. Table IX gives the composition of the media and the results. It will be seen that each vitamine was tested in two different concentrations of asparagine, and then with high additional phosphate. Vitamine 334, which in all previous tests had shown only vegetative activity, could not induce reproduction with any change in the nitrogen and phosphorus supply that was tried. The other vitamine preparations, which had previously been shown to promote reproduction, could not be made to lose this activity by varying the nitrogen and phosphorus supply. When combinations of two preparations were tried, the reproductive factor was suppressed in all cases except in that in which the reproductive vitamine was in excess.

Discussion.

It has been conclusively demonstrated that *Sclerotinia cinerea* cannot thrive on a medium that does not contain at least a certain proportion of the extract from some plant or animal material. These materials do not supply the previously recognized nutrient factors, such as salts, nitrogen, and energy. The facts point to the existence in the plant and animal extracts of a substance similar in nature to the now well-recognized vitamine B of the higher animals. Further examination reveals the fact that this substance has at least one characteristic in common with vitamine B: its adsorption by fullers' earth in an acid medium, and its release again in an alkaline medium. Furthermore, preparations from the conventional sources of vitamine B are found to be potent towards *Sclerotinia*. These coincidences point to the possible identity of the vitamine for the animals and the vitamine for the fungus.

The tests shown in Table IV of the vitamine preparation from the leaves and buds of plants, seeds, seed sprouts, tuber sprouts, rice polish, sporophores and mycelia of fungi, the mycelium of *Sclerotinia* itself, pollen of maize, fruit juices, wort, autolyzed yeast, milk, and pancreatin, show two outstanding features: One is that every material examined furnishes a substance which activates the growth of *Sclerotinia*. The other is that most of the materials enable only vegetative growth to take place, while

a few enable the fungus to sporulate as well. These results, together with the properties of the vitamine as described in the preceding pages, leads to the consideration of two distinct lines of evidence: one for the existence of two vitamins, and one for the existence of only one.

The following points can be enumerated in favor of the two-vitamine hypothesis: (1) There is a considerable body of evidence to show that the reproductive factor is more readily adsorbed by fullers' earth in an alcoholic medium, while the vegetative factor is more readily adsorbed in an aqueous medium. Materials demonstrated to give rise to both activities, *e. g.*, autolyzed yeast and peach decoction, will yield preparations stronger in the one activity or in the other, depending on the medium used in the preparation (Table V). (2) There is some evidence that prolonged high temperatures destroy the vegetative factor more quickly than the reproductive (Table VI). (3) A vitamine preparation which, on the ordinary medium, induces only vegetative growth, cannot induce reproduction also by changes in the proportions of the nutrients, at least so far as the latter have been tried. And a preparation that exhibits both factors on the normal medium has not been made to lose the reproductive factor by changes in the medium, provided the latter will still allow fairly good vegetation to take place (Table IX, Figs. 7 and 8).

From the standpoint of the presence of two vitamins, it is seen that, although growth can apparently take place with only the vegetative factor present, reproduction cannot take place unless both factors are present, since a certain amount of mycelium is necessary to support the reproductive tissue. This is clear from an inspection of Table IX, Cultures 514-518; it is also shown in a large number of other cultures throughout the experiments, by the appearance of reproduction on the larger additions of vitamine more frequently than on the lower additions. The amounts of vegetation indicated in the two columns of Table IX do not differ greatly; but the greater additions of vitamine were necessary to support the heavy reproduction activities. The growths throughout the 0.3 cc. column are about the same, but the growths in the 2 cc. column are noticeably smaller in the 3 middle cultures where the heavy reproduction took place. Although in both amounts of added vitamine the 2 factors are in the same proportion, it is conceivable that the vegetative factor must build up a certain amount of mycelium, with presumably a certain storage of materials, before the reproductive factor can come into play. If the latter factor is absent, vegetative growth will continue until some limiting factor enters in—it may be nitrogen, sugar, its own vitamine, or even old age. If the reproductive factor is present, it constitutes a limiting factor on vegetation by making heavy demands on the mycelium for materials with which to build the spores. Coons¹ draws a

¹ G. H. Coons, *J. Agr. Res.*, 5, 713 (1916).

vivid picture of the struggle that takes place in *Plenodomus* between the vegetative and the reproductive tendencies; he calls vegetation static, because it stores energy, and reproduction dynamic because it releases energy. Klebs always speaks of reproduction and vegetation as being opposed to each other. Coons, to his knowledge, was not speaking in terms of vitamins, nor was he dealing with them, but the phenomena in the two fungi are similar. There is just so much material, carbon, and nitrogen material in the medium available for purposes of construction; whether this is converted into the one kind of tissue or the other in *Sclerotinia* may depend upon the relative activities of the two vitamins involved. The ease with which one or the other vitamin can carry on its own activity depends to a certain extent on the total and relative supplies of nutrients, but the differences are quantitative and not qualitative.

The above experiments furnish evidence that the shuffling of the nitrogen and sugar constituents of the medium will not of itself determine the occurrence or non-occurrence of reproduction in *Sclerotinia*. Both vitamin factors must be present if reproduction is to occur. However, there also must be a proper balance of the other constituents, or sporulation may not take place, probably because the mycelium must have a certain minimum storage of reserve food before it can support reproductive tissue.

On the other hand, certain of the above experiments and observations are more explainable on the hypothesis of a single vitamin. In the first place, since yeast growth is activated both by those preparations which promote only vegetation in *Sclerotinia* and by those which promote both vegetation and reproduction, but is activated more by the latter than by the former, it appears as if a single vitamin were active in all the preparations, although in different degrees.

In the second place, the materials which furnish the reproductive factor in greatest abundance are pollen, fungus sporophores, yeast, peach juice, and the terminal buds of *Phaseolus multiflorus* (Table IV). With the exception of the fruit tissue, these are all tissues characterized by high metabolic activities. In the case of the pollen and of the fungus spores, they are capable of great independent growth; and the yeast, when provided with proper nourishment, has the power of extremely rapid cell division and growth. Now, the one phenomenon which is common to all living tissues and which varies in intensity according to what we are wont to turn "high" or "low metabolic activity," whether the tissue be secretory, growing, muscular, or what not, is respiration. All the materials examined for vitamin were, at one time at least, living materials; and as such must have exhibited respiration in greater or less degree. The tissues which must have been characterized by the greatest respiratory activity, either actual or potential, are those which are found

to contain the most vitamine—pollen, fungus spores, yeast, terminal buds. Osborne and Mendel¹ have found that liver, heart muscle, kidney, brain, and skeletal muscle contain vitamine B in decreasing quantities in the order named; and that the leaves of spinach, alfalfa, clover, cabbage, and timothy are fairly high in the vitamine. Voegtlin and Myers² recently showed that the embryos of the wheat and maize kernels contain all the vitamine, the endosperms containing none. Dutcher³ found that the catalase content of the organs of pigeons fell very low during polyneuritis, but rose again very rapidly when vitamine was fed.

All the above observations point to the conclusion that there is some direct relation between the respiratory activity of a tissue and its content, and, probably, requirement also, of vitamine.

With this in mind, we may think of *Sclerotinia* as having its life phases governed to a certain degree by the supply of vitamine at its disposal. With a meagre supply, vegetation only will take place; with a more plentiful supply, reproduction as well will be possible. Reproduction in this case is simply a modified vegetation. A vegetative hypha grows vertically from the mycelium, and is pinched off into a chain of spores containing a concentrated supply of reserve food. These spores are capable of great independent growth, that is, they contain sufficient reserve supply to enable them to germinate in distilled water and produce hyphae which aggregate several hundred times the volume of the original spores. We can readily believe that to do this the spore must have considerable vitamine stored within it. Hence the mother hypha must have had at its disposal abundant vitamine, and hence, also, the more abundant the vitamine in a medium, other factors being suitable, the more abundant will be the sporulation.

This hypothesis of a single vitamine leaves unexplained, of course, the failure to secure qualitative differences in the vegetation-reproduction ratio by changes in the proportions of nutrients; and it fails to accord with the different degree of adsorbability on fullers' earth in alcoholic and in aqueous media. Nevertheless, in the light of all the facts available, both in these experiments and in those of others, the idea of a single vitamine for normal metabolism in *Sclerotinia* is more plausible than that of two vitamins.

As regards the identity of this vitamine, the evidence so far is not very clear. It can probably be found in almost all plant and animal materials. Vitamine B, the only well-known vitamine that bears any similarity to the one in question, has been found in a great many plant and animal

¹ T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 34, 17 (1918); 37, 187 (1919).

² C. Voegtlin and C. N. Myers, *Am. J. Physiol.*, 48, 504 (1919).

³ R. A. Dutcher, *J. Biol. Chem.*, 36, 63 (1918); R. A. Dutcher and F. A. Collatz, *Ibid.*, 36, 347 (1918).

tissues, although in some of them, notably in polished rice and in the endosperm of wheat, it is in very small amounts, or even absent. This apparent universality of vitamine B and of the *Sclerotinia* vitamine, their behavior towards fullers' earth, and the fact that materials very high in the B factor (yeast, pollen,¹ barley malt) have also furnished some of the most active preparations for *Sclerotinia*, argue for the identical nature of the two vitamins. It is on these bases that Williams believes that his yeast vitamine is also vitamine B. However, we cannot come to a definite conclusion at present concerning the identity of the vitamine for *Sclerotinia*. A much wider search for sources of the vitamins, and more effective separations of them, must first be made.

The writer wishes to acknowledge at this place the helpful criticism and suggestions of Professor William Crocker, under whose direction the foregoing work was done.

VI. Summary.

A review of the existing literature on vitamins reveals the probability of their universal occurrence in the organic world. Phenomena of vitamin-like origin have been recorded for the mammals, the birds, the seed-plants, the fungi, and the bacteria. Many other phenomena of animal and plant life, especially of the parasitic fungi, not as yet connected with vitamins, lend themselves to a vitamin explanation.

Sclerotinia cinerea, the brown rot fungus of peaches and plums, cannot grow on a medium made up of sucrose, salts, and asparagine. The addition to this medium of small amounts of plant decoctions, especially of the fruits of plums and peaches, induces growth. The experiments in the foregoing paper show that the factor furnished by the plant decoction is not one of mineral, nitrogen, or energy requirements, but is of the nature of a vitamin.

By means of adsorption onto fullers' earth, vitamin preparations were made from a large number of widely scattered sources, both plant and animal. All of these preparations were active in promoting growth in *Sclerotinia*. A few of them would promote reproduction as well.

Experiments designed to show whether two separate vitamin factors are involved in these two phases, vegetation and reproduction, in the life history of *Sclerotinia* yielded some evidence favoring this view: (1) the reproductive element is adsorbed by fullers' earth more readily in an alcoholic, and the vegetative element more readily in an aqueous, medium; (2) some sources yield preparations which predominate in the vegetative factor, others yield preparations that promote both activities; (3) preparations which promote only vegetation on a normal medium have not been induced to promote reproduction by changes in the proportions of the nutrients in the medium; and preparations that, on normal media

¹ R. A. Dutcher, *J. Biol. Chem.*, 36, 551 (1918).

promote both activities, have not been made to lose entirely the reproductive element, thus indicating that the influence of the nutrients in affecting the ratio of vegetation to reproduction is quantitative and not qualitative.

On the other hand, the hypothesis of the existence of but a single vitamine for *Sclerotinia* is more plausible, according to much of the experimental evidence. It is very probable that reproduction in *Sclerotinia* is simply a different manifestation of the same activities as characterize vegetation. The single activity that is apparently most dependent on a vitamine supply is respiration. Respiration is common to all the materials which have yielded the vitamine; and the degree of metabolic, and hence respiratory, activity in these materials is proportional to the activity of the vitamine prepared from them. Thus the evidence is accumulating in favor of the view that there is a close connection between respiration in a cell and its vitamine content, and also its vitamine requirement. Just which cells in the plant world can synthesize this vitamine is still an open question. The *Sclerotinia* vitamine is possibly identical with the water-soluble B of the higher animals; and since the latter cannot synthesize this vitamine, it becomes an important point to know which plant organs can.

ST. PAUL, MINNESOTA

THE MECHANISM OF THE REACTION BETWEEN ETHYLENE AND SULFUR CHLORIDE.¹

BY J. B. CONANT, E. B. HARTSHORN AND G. O. RICHARDSON.

Received December 18, 1919

I. Introduction.²

When ethylene gas is led into rapidly agitated sulfur monochloride at a temperature of 40° to 60°, β,β -dichloro-ethylsulfide and sulfur are formed. This may be represented by the following equation:



The following mechanisms of the reaction are possible: (1) the reaction may take place by the simultaneous action of two molecules of ethylene and one of sulfur monochloride; (2) one molecule of sulfur monochloride may react with one molecule of ethylene to give the intermediate compound $\text{CH}_2\text{ClCH}_2\text{S}_2\text{Cl}$, which then may react further with ethylene to give dichloro-ethylsulfide and sulfur, or a disulfide, $(\text{CH}_2\text{ClCH}_2)_2\text{S}_2$.

¹ Published by permission of the Director of the Chemical Warfare Service.

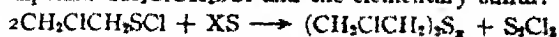
² The work presented in this paper was incidental to an investigation of an important war problem. As other matters were of greater moment, an exhaustive study of the mechanism of this reaction was impossible. It is believed, however, that the present incomplete results are of sufficient interest to warrant publication. An investigation of the same general problem from a different angle is planned.

may be formed which subsequently loses sulfur to yield the sulfide; (3) an intermediate compound, $\text{CH}_2\text{ClCH}_2\text{SCl}$, and sulfur may be the first products of the reaction; this intermediate may then unite with more ethylene. It is evident that if the speeds of the 2 successive reactions, suggested in (2) and (3), are equal throughout the reaction, the conditions will be experimentally those represented by (1), but if the speeds are different, an intermediate compound will be present in varying amounts during the reaction.

It has been possible to show by freezing-point determinations that the reaction does proceed in two stages. However, it has been found difficult to obtain conclusive evidence as to the exact structure of the intermediate product. A study of the reaction between sulfur dichloride and ethylene has thrown some light on this point. Further evidence has also been obtained from a study of the by-products of the sulfur monochloride reaction.

Sulfur dichloride combines rapidly with one molecule of ethylene and the product is apparently $\text{CH}_2\text{ClCH}_2\text{SCl}$. This is an unstable substance which combines further with ethylene producing some dichloroethylsulfide. It easily decomposes on warming, producing thick, black oils and hydrogen chloride. This decomposition is accelerated by metals and metallic salts. If the reaction between ethylene and sulfur monochloride is stopped when about half completed, the product behaves in exactly the same manner. It also decomposes into hydrogen chloride and high boiling substances. It thus seems probable that the intermediate compounds are the same in the case of both sulfur dichloride and sulfur monochloride.

The intermediate substance $\text{CH}_2\text{ClCH}_2\text{SCl}$ reacts with sulfur on warming and produces some complex sulfur compounds as the sulfur disappears. An examination of the by-products from the sulfur monochloride reaction has shown that they are polysulfides. The formation of these compounds we believe to be due to the interaction of the intermediate compound $\text{CH}_2\text{ClCH}_2\text{SCl}$ and the elementary sulfur.



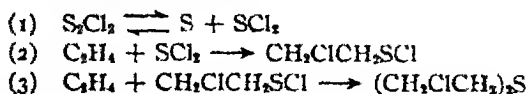
An analogous reaction is reported as taking place when CCl_4SCl is heated with sulfur; $\text{C}_2\text{Cl}_6\text{S}_2$ and $\text{C}_2\text{Cl}_6\text{S}_3$ are among the products.¹

Under certain conditions the final product of the monochloride reaction is a clear, yellow, liquid containing no precipitated sulfur. All the sulfur set free in the reaction is held in colloidal solution. The sulfur slowly separates from this solution on standing or may be quickly thrown down by warming for a few hours at $110^\circ\text{--}120^\circ$. The freezing point of the material is not changed by the precipitation of the sulfur. This clearly shows that the sulfur is present in colloidal solution. The final products

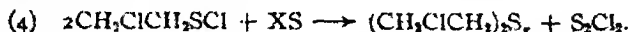
¹ Klason, *Ber.*, 20, 2378 (1887).

of the reaction are thus, dichloro-ethylsulfide, free sulfur (often in colloidal solution) and 15 to 25% of complex polysulfides.

In view of all these facts it seems that the reaction between sulfur monochloride and ethylene can be best represented by the following equations:



and a side reaction



If this mechanism is correct the ethylene reacts only with the small amount of sulfur dichloride in equilibrium with the monochloride.¹ The sulfur dichloride is continually removed by Reaction 2 and this causes Reaction 1 to go to completion. As the concentration of the intermediate compound increases it begins to react more rapidly with ethylene, according to Equation 3. This reaction only becomes appreciable when about 30% of the total ethylene has been absorbed (Fig. 3). Towards the end of the process, however, this reaction predominates as the concentration of the intermediate compound is now high and that of sulfur chloride low. The concentration of dichloro-ethylsulfide then increases rapidly until the reaction is complete.

II. Proof that the Reaction Proceeds in Two Stages. Freezing-Point Curve of Dichloro-ethylsulfide.

Pure dichloro-ethylsulfide freezes at 13.9°. The presence of impurities, of course, lowers the freezing point. This depression is approximately equal for impurities of about the same molecular weight. Fig. 1 shows a curve plotted from the results of experi-

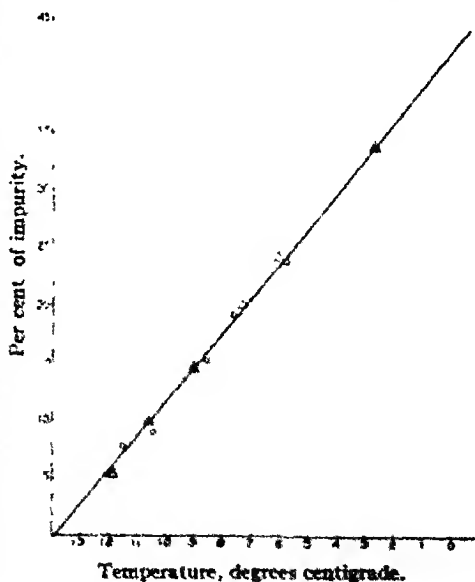


Fig. 1.

¹ There is some evidence to indicate that sulfur monochloride is in equilibrium with the dichloride and sulfur. For example, the monochloride when carefully purified is light yellow but on warming becomes a bright red which is characteristic of dilute solutions of the dichloride.

ments on the freezing point of mixtures of dichloro-ethylsulfide and carbon tetrachloride (m. w. = 154) and dichloro-ethylsulfide and trichloro-ethylsulfide (m. w. = 193). The points fall close together.

The melting-point determinations were taken in the usual form of apparatus used for determining the molecular weight by the freezing-point method. A standardized tenth-degree thermometer was used. The freezing point was always determined as the solidified mass gradually warmed up and the thermometer was read when the last portion of the solid dichloro-ethylsulfide was in equilibrium with the liquid. There was very little difficulty in obtaining consistent results with samples which did not contain more than 20% of impurity.

The curve shown in Fig. 1 easily enables one to determine the amount of any impurity in dichloro-ethylsulfide by determining the freezing point. The following table indicates the accuracy of the method. Samples containing known weights of dichloro-ethylsulfide and dichloro-propylsulfide were made up and their freezing points determined. The last two columns show the percentage composition as known from the weights of pure materials taken and as determined by the freezing point

TABLE I

Sample	Freezing point °C	Dichloro-propylsulfide impurity %	Dichloro-propylsulfide determined from freezing point %
1 . . .	8.5	15.0	15.3
2 .	8.6	15.5	16.0
3 .	6.5	22.3	22.1
4 .	5.0	26.4	26.4

Analysis of the Reaction Mixture.

The determination of the freezing point of dichloro-ethylsulfide furnished an easy method for studying the progress of the reaction between ethylene and sulfur monochloride. Samples were withdrawn from the reaction mixture from time to time and added in known amounts to pure dichloro-ethylsulfide. The freezing point of the resulting mixture was then determined, and from the curve the per cent. of foreign material in this mixture was determined. If this per cent. was the same as the per cent. of the reaction mixture added to the pure dichloro-ethylsulfide, then the reaction mixture contained no dichloro-ethylsulfide. If it was less, then the difference was obviously due to dichloro-ethylsulfide present in the reaction mixture. Thus, by a very simple calculation, it was possible to determine how much dichloro-ethylsulfide had been formed in the reaction up to the time that the particular sample was taken. The weights of sample and pure dichloro-ethylsulfide were always taken so that a freezing point of from 5° to 9° was observed. In this range the maximum error in the determination of the percentage composition is about one part in 15. This means that the error in determining the composition

of the reaction mixture was of about the same order. The values given in the following table are, therefore, only accurate to about 10%. They, nevertheless, are entirely satisfactory in showing the progress of the reaction, and clearly show that the reaction proceeds in 2 stages

In Table II the results of two different runs are shown. In each run about 300 g. of sulfur monochloride was used; the temperature was kept between 50 and 60°. The first column gives the per cent. of the total ethylene absorbed when the sample was taken; the second column

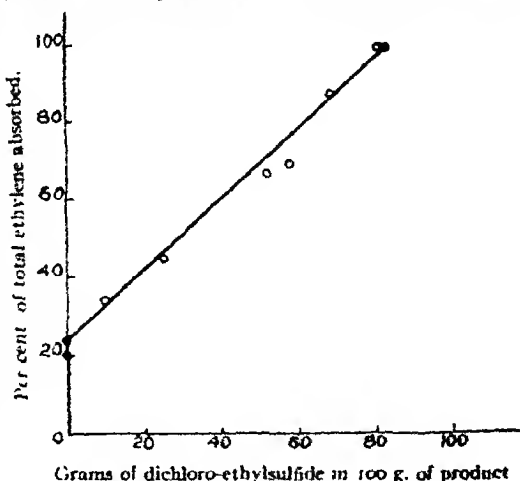


Fig. 2

shows the number of grams of dichloro-ethylsulfide in 100 g. of this reaction mixture, the third column gives the amount which would have

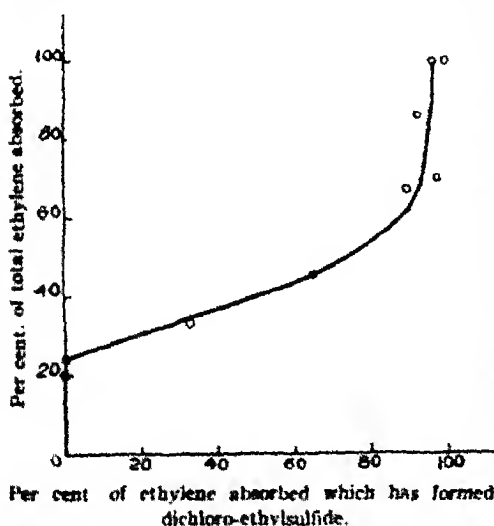


Fig. 1

been present if all the ethylene absorbed up to that point had formed the sulfide; the fourth shows the relationship between the actual amounts of dichloro-ethylsulfide and the amount corresponding to the ethylene absorbed. Inasmuch as the theoretical amount of ethylene is never absorbed and the amount of dichloro-ethylsulfide in the final product is never 100%, the values in Col. 3 are somewhat different from the amounts based on the simple equation:



The values in Col. 2 are plotted against those in Col. 1 in Fig. 2.

the values in Col. 4 against the same variable in Fig. 3. The figures in Col. 4 obviously show what portion of the ethylene absorbed has produced dichloro-ethylsulfide.

TABLE II.

Total ethylene absorbed. %	Dichloro-ethylsulfide in 100 g of reaction mixture. G	Dichloro-ethylsulfide in 100 g if all C_2H_4 had formed the sulfide G.	Relationship between actual dichloro-ethylsulfide and amount calculated from C_2H_4 absorbed. %.
Run I			
19.7	0.0	16.9	0.0
34.1	9.6	20.3	32.8
70.0	58.6	39.9	97.8
100.0	82.3	85.8	95.9
Run II.			
23.8	0.0	20.6	0.0
55.0	25.5	39.1	65.2
67.25	52.6	58.4	90.1
87.5	70.1	76.0	92.2
100.0	84.9	86.9	97.7

It is evident from these results that even after 23.8% of the ethylene had been absorbed, *there was no dichloro-ethylsulfide present in the reaction mixture.* The curve shown in Fig. 3 is the most instructive, as it clearly shows the course of the reaction. Between the start and about 30% absorption an intermediate compound is being formed entirely; when its concentration has become sufficiently high, it now begins to react with ethylene to produce dichloro-ethylsulfide. By the time that 60 or 70% absorption has been reached the 2 reactions are proceeding at very nearly the same rate since the concentration of the intermediate compound is now high and that of the sulfur chloride low. The result is that during the last part of the reaction the ethylene, as fast as it is absorbed, is converted into dichloro-ethylsulfide.

III. Evidence from the Action of Sulfur Dichloride and Ethylene.

Dichloro-ethylsulfide is formed in small amounts when ethylene is bubbled through sulfur dichloride at a low temperature. The main product is a more highly chlorinated sulfide formed by the interaction of sulfur dichloride and dichloro-ethylsulfide. This side reaction can be avoided by working with dilute solutions of sulfur dichloride in carbon tetrachloride and in this way a fairly pure product can be obtained. A study of the rate of absorption of ethylene by sulfur dichloride led to the belief that this reaction proceeded in two stages. The intermediate compound can be prepared in a fairly pure state by allowing cold sulfur dichloride to come quickly in contact with an excess of ethylene.

The Intermediate Compound.

A 20-liter bottle, fitted with a manometer and a dropping funnel, was filled with ethylene. About 10 g. of sulfur dichloride (prepared accord-

ing to the method of Beckmann¹⁾ was introduced into the bottle which was then shaken in a large ice bath for a few moments. The reaction between the dichloride and the gas was very rapid as noted by the change in the pressure. The amount of ethylene absorbed was a little less than one molecule for every molecule of sulfur dichloride. The product was a light yellow liquid which on continued agitation slowly absorbed more ethylene. Several analyses of the liquid corresponded to the formula $\text{CH}_2\text{ClCH}_2\text{SCl}$; the sulfur content averaged about 1% too low, the chlorine content about 1% too high. This indicates the presence of a somewhat more highly chlorinated impurity.

The intermediate compound was very unstable. It slowly evolved hydrogen chloride even at 0° and when warmed to 50° this evolution became rapid. At this temperature the compound was changed into a thick, black oil in the course of 3 or 4 hours. This decomposition was greatly accelerated by the presence of metallic iron or a trace of anhydrous ferric chloride. In the presence of these catalysts the decomposition was very rapid even at 5° .

The intermediate compound reacts with elementary sulfur if the two substances are warmed together for a short while. The sulfur apparently enters into the organic molecule as the product is completely soluble in 3 times its volume of carbon tetrachloride. The product is a black, thick oil which is probably a polysulfide since on oxidation with nitric acid it yields sulfuric acid and some organic sulfonic acid which was not identified. It closely resembles, in this respect, and in physical appearance, the polysulfides obtained as by-products in the monochloride reaction (see below).

Comparison of the Intermediate Compound and the Reaction Mixture Obtained from the Monochloride.

Sulfur monochloride which has absorbed *one molecule* of ethylene behaves very much like the intermediate compound prepared from sulfur dichloride and ethylene. On standing a few hours at room temperature this product rapidly gives off hydrogen chloride and passes into a thick, black oil. This decomposition is accelerated by the presence of iron and iron salts as is the decomposition of the compound $\text{CH}_2\text{Cl}-\text{CH}_2\text{SCl}$. Because the incomplete reaction mixture from sulfur monochloride always contains unchanged sulfur chloride and dichloro-ethylsulfide as well as an intermediate compound, no pure substance could be isolated for a more direct and convincing examination.

IV. Side Products of the Monochloride Reaction.

The amount of elementary sulfur usually formed by the action of ethylene on sulfur monochloride is only about 50% of the amount correspond-

¹ *Z. physik. Chem.*, 65, 289 (1909).

ing to the dichloro-ethylsulfide actually obtained. The yield of the dichloro-ethylsulfide based on the monochloride employed is only about 80%, although the amount of ethylene absorbed corresponds to about 95% of that theoretically required. The sulfur monochloride and ethylene which do not form dichloro-ethylsulfide are combined together with the "missing sulfur" in the form of a non-volatile organic material.

Non-Volatile Residue.

This material, which is present to the extent of 15 to 25%, is left behind in the vacuum distillation of the crude dichloro-ethylsulfide. It is a thick, black tar which often contains some elementary sulfur. The elementary sulfur can be readily separated by treating the material with carbon tetrachloride, filtering off the sulfur and evaporating the solvent. The organic material in the residue is soluble in carbon tetrachloride, benzene, chloroform and carbon disulfide; it is insoluble in ether, alcohol and water; $d_{25} 1.45$ to 1.47 . Since this black tar is completely soluble in the solvents just mentioned it must contain very little if any elementary sulfur. Judging from the amounts of ethylene and sulfur monochloride which do not appear as dichloro-ethylsulfide and the amount of sulfur unaccounted for, this material should contain 55 to 60% of sulfur and 20 to 25% of chlorine; a sample actually analyzed gave the values $S = 57\%$, $Cl = 22\%$. While there is every reason to believe the material contains several substances (including probably some free carbon and complex products formed at the temperature of distillation) it is nevertheless interesting to compare its composition with the formulas for various polysulfides.

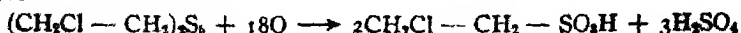
Formula:	S, %	Cl, %
$(CH_2Cl-CH_2)_2S_4$	50	28
$(CH_2Cl-CH_2)_3S_4$	55	25
$(CH_2Cl-CH_2)_4S_4$	60	22

It is evident that the mixture has the approximate composition of the pentasulfide. It is shown below that it is probable that the material consists very largely of this substance.

Oxidation of the Residue.

Cold conc. nitric acid readily oxidizes the material to a water-soluble product. A small amount of sulfur is left unattacked—this probably is the elementary sulfur which was present in solution in the material; it amounts to about 1%. An aqueous solution of the oxidation product contains sulfuric acid and an organic sulfonic acid containing chlorine. The sulfuric acid was removed as insoluble barium sulfate and the barium salt of the organic acid obtained in 2 experiments corresponded to a content of sulfur in the original material of 31.6 and 32.1%. If the substance were the pure pentasulfide and were oxidized according to the fol-

lowing equation, the amount of sulfur oxidized to sulfuric acid would be 34%:



The barium salt of the sulfonic acid could be recrystallized from alcohol. It contained carbon, sulfur and chlorine as well as barium. The identification of this salt was not undertaken because of the lack of time and material. It was probably the barium salt of $\text{CH}_2\text{ClCH}_2\text{SO}_3\text{H}$. The formation of sulfuric acid by the oxidation proves that the compound must contain a polysulfide linkage $-\text{S}-\text{S}-$ and the formation of an organic sulfonic acid shows the presence of the linkage $-\text{C}-\text{S}-\text{S}-$. No sulfone or sulfoxide was obtained. The amount of sulfuric acid formed indicates that the material is the pentasulfide.

It is interesting to note that Guthrie¹ investigated the action of ethylene on sulfur monochloride at 100° and obtained a thick oil, d. 1.346. This material he did not purify or identify carefully but assumed it to be $\text{CH}_2\text{ClCH}_2\text{SSCH}_2\text{Cl}$ (interpreting his formulas in modern terms). Spring² repeated this experiment and oxidized the material to $\text{CH}_2\text{ClCH}_2\text{SO}_3\text{H}$ which he identified. He gives no quantitative data as to the amount of acid formed by the oxidation. Undoubtedly both Guthrie and Spring were working with a mixture of polysulfides very similar if not identical with the material we are considering. The effect of a higher temperature on the reaction between ethylene and sulfur chloride leads to blackening and the formation of a large amount of the side products.

Decomposition with Steam.

If steam is passed through the polysulfides heated to somewhat above 200° , a small amount of yellow oil gradually distills. The residue in the flask on cooling is a black, brittle mass, an analysis of it showed that it contained 62% of sulfur and 0.2% of chlorine. This material is, unlike the parent substance, only partially soluble in carbon tetrachloride. On heating in a small tube, sulfur vapors are given off in large quantities, and sulfur deposits on the walls of the tube. The material evidently contains large amounts of elementary sulfur.

The yellow oil can be distilled in vacuum, but with considerable decomposition. It has a boiling point corresponding to $170-210^\circ$ at atmospheric pressure. It is evidently a decomposition product of the original material. The analysis of two portions follow:

Low boiling fraction $170-180^\circ$ at 760 mm.

Calc. for disulfide: S, 33.5; Cl, 37.2. Found: S, 34.0; Cl, 34.4.

High boiling fraction $180-210^\circ$ at 760 mm.

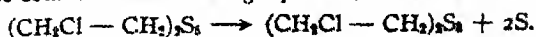
Calc. for trisulfide: S, 43.0; Cl, 31.8. Found: S, 40.7; Cl, 32.9.

On oxidation with nitric acid it yielded sulfuric acid and an organic sul-

¹ Ann., 216, 234 (1860).

² Bull. soc. chim., 42, 629 (1887).

acid containing chlorine. A quantitative oxidation of the higher boiling material gave an amount of barium sulfate corresponding to 12% of sulfur. If the material were the trisulfide the amount would be 14.4%. The amount of sulfur left in the black, brittle residue just spoken of corresponds to 20% of the original material. If the formation of the oil followed the course of the following equation, the amount would be 22%:



It is thus certain that the oil is a polysulfide and is formed from the original polysulfide by the action of steam at a high temperature, elementary sulfur being set free. It is probably largely the trisulfide. A similar transformation has been recorded with ethyl tetrasulfide. This compound, when treated with steam at a high temperature, is said to give ethyl trisulfide and free sulfur.¹ The tetrasulfide when heated with free sulfur gives the pentasulfide. Apparently the organic polysulfides like the inorganic can take on or lose additional sulfur atoms quite readily.

Probable Constitution of the Non-Volatile Material.

All the experimental evidence given above shows clearly that the residue left after the vacuum distillation is a mixture of organic polysulfides, probably consisting largely of $(\text{CH}_2\text{Cl} - \text{CH}_2)_3\text{S}_3$. An additional piece of evidence is found in the fact that on chlorination sulfur chloride and hexachloro-ethane are formed. The following considerations show that this organic material is actually present in the crude product and is not formed during the distillation. The best crude dichloro-ethylsulfide obtained by the sulfur-monochloride process has a melting point corresponding to the presence of 10% of an impurity of a molecular weight of about 150. (The polysulfides having a much higher molecular weight would be present in larger amounts for a given melting point.) The melting point of the material is changed only a few tenths of a degree by heating the substance several hours at 120°. This shows that very little reaction takes place at this temperature. The residue from the vacuum distillation when mixed with dichloro-ethylsulfide, in the proportion in which it is obtained, lowers the freezing point to that of the original crude material. It is evident that very little if any change has taken place in the non-volatile impurity during the distillation. This evidence does not, however, rule out such a change as might take place between the polysulfides and elementary sulfur which is present to a certain extent in solution, in suspension and in "colloidal solution." The tetrasulfide might, during the vacuum distillation, take up another atom of sulfur forming the pentasulfide. This change since it does not involve the dichloro-ethylsulfide and only changes the molecular weight of the impurity about 10% would not be detected by the freezing-point methods just discussed.

¹ *J. prakt. Chem.*, [2] 15, 214 (1877).

Summary.

1. The reaction between sulfur monochloride and ethylene proceeds in two stages. The course of this reaction has been followed by a method of analysis based on freezing-point determinations.
2. It is probable that the intermediate compound is $\text{CH}_2\text{ClCH}_2\text{SCl}$. A similar intermediate product has been obtained in impure condition by the action of sulfur dichloride on ethylene.
3. 15 to 20% of non-volatile side products are always formed in the monochloride reaction. These side products are organic polysulfides.

WASHINGTON, D. C

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

THE GOLD NUMBERS OF PROTALBINIC AND LYSALBINIC ACIDS.¹

BY ROSS AIKEN GORTNER

Received December 29, 1919

In 1902 Paal² prepared 2 substances by the action of sodium hydroxide upon egg albumin which he regarded as definite compounds. To these substances he gave the names of "protalbinic" and "lysalbinic" acids. These preparations exert a strong protective or stabilizing action when added to suspensions. From the statements which occur in the textbooks one would assume the protective action of these materials to be of the highest order. Thus Freundlich³ states "Peptone solutions are so slightly colloidal that they have no protective action whatever. On the other hand, protalbinic and lysalbinic acids possess unusual ability to hold the most varied kinds of finely divided materials in colloidal solution." Taylor⁴ states, "Paal's protalbinic acid and lysalbinic acid are extremely active protectors," and Bechhold⁵ concludes that "Peptones have no protective action at all whereas some of the albumoses, especially sodium lysalbinate and sodium protalbinate have a very powerful protective action."

In view of these statements it appeared to be rather surprising that no exact measure of their value as protective colloids appeared in the litera-

¹ Presented before the Division of Biological Chemistry at the Cleveland meeting of the American Chemical Society, Sept. 9-13, 1918. Published with the approval of the Director as Paper No. 189, Journal Series, Minnesota Agricultural Experiment Station.

² C. Paal, *Ber.*, 35, 2195-2206 (1902).

³ Freundlich, H. "Kapillarchemie," Leipzig, 1909, p. 431.

⁴ W. W. Taylor, "The Chemistry of Colloids," Longmans, Green & Co., N. Y., 1913, p. 130.

⁵ H. Bechhold, "Colloids in Biology and Medicine," translated by J. G. M. Bullock. Van Nostrand Co., N. Y., 1916, p. 86.

ture with the exception of a statement by Zsigmondy¹ that the sodium salt of protalbinic acid had a gold number of 0.03-0.08 and that of lysalbinic acid 0.02-0.06. The gold numbers of various other protective colloids are given in almost all of the colloid texts. From the statements noted, one would infer that protalbinic and lysalbinic acids exceeded all of the usually available materials in their protective value.

Inasmuch as we possessed a quantity of highly purified protalbinic and lysalbinic acids prepared for another purpose, it was thought advisable to make a careful determination of their relative value as protective colloids, utilizing as a measure the gold number of Zsigmondy.² The preparation of our protalbinic and lysalbinic acids has already been described.³ In determining the gold number, a weighed amount of the "acid" was brought into solution in water by the cautious addition of 0.0714 *N* sodium hydroxide solution, taking care that no more alkali was added than was required to effect complete solution. Only a very small quantity of alkali was needed to peptize the preparations, so that the gold numbers which I obtained are not necessarily comparable with those which Zsigmondy found for the sodium salts of the acid, but are more nearly a measure of the protective value of the organic radical. The presence of additional alkali would undoubtedly alter the gold numbers which I obtained, due to the well known stabilizing effect of the hydroxyl ion. After making up to definite volume, this solution, or a dilution made from it, was used at once in the tests. The gold number determination, including the preparation of the red gold sol, was carried out exactly as described by Schulz and Zsigmondy.⁴ In order to check the values obtained with those of other workers, the gold numbers of a number of other materials were likewise determined. The values obtained are shown in Table I. The values given by Zsigmondy⁴ are also included.

It will be noted that in the cases of gelatin, egg albumen and gum arabic, my values are in good agreement with those of other workers. The sample of sodium oleate which I used had been in stock for a long time and has a somewhat rancid odor, which may explain my high values. At any rate, it would appear as if my values were reliable for the materials

¹ R. Zsigmondy, "The Chemistry of Colloids," translated by E. B. Spear. Wiley and Sons, N. Y., 1917, p. 212. This statement of Zsigmondy was not known to me until long after my work was completed. The figures are not given in his tables of comparative gold numbers nor is the reference indexed so as to be readily found.

² R. Zsigmondy, *Z. anal. Chem.*, 40, 697-719 (1901).

³ C. Kennedy and R. A. Gortner, "The Nitrogen Distribution in Protalbinic and Lysalbinic Acids," *THIS JOURNAL*, 39, 2734-2736 (1917).

⁴ Fr. N. Schulz and R. Zsigmondy, *Beitr. Chem. Physiol. Pathol.*, 3, 137-160 (1903).

⁵ R. Zsigmondy and E. B. Spear, "The Chemistry of Colloids," Wiley and Sons, N. Y., 1917, p. 107.

TABLE I.
Gold Numbers of Various Emulsoid Colloids.

Substance	Gold number	
	Goriner	Zeigmondy ^a
Dextrin (British gum)	125-150	
Soluble starch.....	10-15	
Sodium oleate.....	2-4	0.4-1.0
Egg albumen..	0.08-0.10	0.15-0.25 (Taylor ^b)
Gum arabic.....	0.10-0.125	0.15-0.25
Protalbinic acid..	0.15-0.20	0.03-0.08 (sodium salt)
Lysalbinic acid.....	0.10-0.125	0.02-0.06 (sodium salt)
Gelatin.....	0.005-0.0125	0.005-0.010

^a R. Zeigmondy and E. B. Spear, *loc. cit.*

^b Taylor, *loc. cit.*

under investigation, and that be the case, we must conclude that the protective action of Paal's protalbinic and lysalbinic acids, as measured by the gold number, has been much over-rated, inasmuch as their gold number is only approximately equal to that of gum arabic and only about $\frac{1}{10}$ that of gelatin.

ST. PAUL, MINN.

[CONTRIBUTION FROM THE ESSENTIAL OILS LABORATORY, DRUG DIVISION, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE CONSTITUTION OF CAPSAICIN, THE PUNGENT PRINCIPLE OF CAPSICUM. II.

By E. K. NELSON

Received December 31, 1919

Since the appearance of the author's first communication¹ on this subject, Lapworth and Royle² have published the results of their work on capsaicin. These investigators are not fully disposed to accept the author's view of the constitution of capsaicin as final, on the ground that "his (Nelson's) conception of capsaicin as an acid amide is not easily reconciled with the somewhat ready reduction of a part of capsaicin to ammonia and an aliphatic alcohol boiling at about 216-217°; its distinctly, basic character and the great stability of the substance toward alkalis are also somewhat difficult to understand." They surmise that "under the energetic conditions used by Nelson internal oxidation or molecular rearrangement would not be surprising."

Proof of the structure of capsaicin is now given by its generation from synthetic vanillyl amine and the decenoic acid previously isolated from capsaicin. The complete synthesis is impossible, of course, until we know the exact structure of the decenoic acid entering into the molecule. In view of the great number of possible isomers and the difficulty

¹ *THIS JOURNAL*, 41, 1113 (1919).

² *J. Chem. Soc. Trans.*, 1116, 1100 (1920).

of locating the double bond in a substance of which only limited quantities are available, the structure of this decenoic acid must remain at present undetermined.

Regeneration of Capsaicin.

5.1 g of decenoic acid (from capsaicin) was converted into the acid chloride by means of phosphorus trichloride and the acid chloride added gradually to a suspension of 9.2 g. of vanillyl amine in dry ether. 5.5 g. of a crystalline, very pungent substance was obtained, which recrystallized from a mixture of petroleum ether with 10% of ether, melted at 65°, and, mixed with capsaicin, showed no depression in melting point. An optical-crystallographic examination by Dr. E. T. Wherry, of this bureau, also showed it to be identical with capsaicin.

Calc for $C_{15}H_{27}NO_2$: C, 70.8; H, 8.8. Found: C, 70.5; H, 9.0

Capsaicin must, therefore, be a vanillyl decenoyl amide.

Vanillyl octoyl amide¹ was boiled for 2 hours with a 50% solution of sodium hydroxide and recovered unchanged. It is somewhat soluble in conc. hydrochloric acid and is precipitated unchanged on the addition of water.

Free vanillyl amine is quite unstable, ammonia being easily liberated from it by boiling with water or solutions of alkali carbonates. Therefore, in an alkaline reduction process, such as the boiling with sodium in ethyl alcohol performed by Lapworth and Royle, any decomposition of the capsaicin taking place would probably result in the liberation of ammonia.

Decenoic Acid.

Attempts to oxidize the decenoic acid from capsaicin by means of chromic acid mixture indicated that several acids may be formed. Owing to the small amount of acid used, no very definite results were obtained.

Fusion with potash splits decenoic acid into acetic acid and an octoic acid. However, this affords no proof of the location of the double bond, as it is well known that potash fusion may cause a displacement of the double bond in unsaturated acids. Acetic acid was identified through its silver salt and the formation of ethyl acetate. The octoic acid obtained has an odor like that of caprylic acid, but differs from the latter in that it remains liquid when cooled in an ice and salt mixture, and boils at about 240–245°. Its silver salt was prepared and found to be difficultly soluble in water.

Calc for $C_{14}H_{26}O_2Ag$: Ag, 43.0; C, 38.2; H, 6.0. Found: Ag, 42.6; C, 38.6; H, 5.8.

Summary.

Confirmation of the structure of capsaicin has been obtained by its regeneration from vanillyl amine and the decenoic acid isolated from capsaicin. Synthetic vanillyl octoyl amide was found to resemble cap-

¹ Nelson, *THIS JOURNAL*, 41, 2124 (1916).

saicin closely in its stability toward boiling conc. sodium hydroxide solution and in its solubility in conc. hydrochloric acid.

The decenoic acid isolated from capsaicin, on fusion with potassium hydroxide, breaks down into acetic acid and an octoic acid with a branched chain.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE USE OF OXALYL CHLORIDE AND BROMIDE FOR PRODUCING ACID CHLORIDES, ACID BROMIDES OR ACID ANHYDRIDES. III.

BY ROGER ADAMS AND L. H. ULICH

Received January 8, 1920.

It has already been pointed out in previous communications that oxalyl chloride in the presence of pyridine¹ is a valuable reagent for the identification of phenols and that its action with aromatic acids² offers a simple method for the preparation of the corresponding anhydrides. This paper contains an extension of the work with oxalyl chloride. The reactions of this substance with various aliphatic and aromatic acids as well as with the sodium salts of such acids are described. Either acid anhydrides or acid chlorides may be obtained, depending upon the conditions and proportions of materials used. Aliphatic and aromatic acid anhydrides and oxalyl chloride give the corresponding acid chlorides. The mechanism of these various reactions is explained. It has been shown also that oxalyl chloride may be used for producing certain inorganic acid chlorides from the corresponding oxides, and for causing the Beckmann rearrangement of various ketoximes. Oxalyl bromide may be employed in the same way as oxalyl chloride and yields with acids or their salts either acid anhydrides or acid bromides. Phosphorus pentabromide and organic acids or phosphorus pentabromide and the salts of organic acids yield acid bromides.

If aromatic or aliphatic acids are warmed with 2.5 moles of oxalyl chloride, these acids are converted quickly and practically quantitatively into the corresponding acid chlorides. The reaction may even be carried out in the presence of benzene as a solvent and very successful results obtained. Various types of acids were chosen for experimentation. The following give excellent yields of acid chloride: benzoic, *p*-bromobenzoic, *o*-bromobenzoic, *n*-valeric, lauric, phenylacetic, hydrocinnamic and salicylic acids. *p*-Hydroxybenzoic acid does not give an acid chloride but instead a complex condensation product. Certain nitro derivatives of benzoic acid react very peculiarly with oxalyl chloride; thus *m*-nitro-

¹ This JOURNAL, 37, 2716 (1915).

² *Ibid.*, 40, 424 (1918).

benzoic, *p*-nitrobenzoic, 3,5-dinitrobenzoic, 2,4,6-trinitrobenzoic acids when treated as described above, all give the corresponding double anhydride of 2 moles of aromatic acid and one mole of oxalic acid. Even on refluxing for several hours with excess of oxalyl chloride, no decomposition of these double anhydrides takes place.

Instead of using the organic acid and excess of oxalyl chloride to produce acid chlorides, it is also possible to use the sodium salts of the organic acids and oxalyl chloride. When one mole of the sodium salt of the organic acid is added gradually to 1-1.5 moles of oxalyl chloride in benzene, the reaction runs smoothly with the production of sodium chloride and the organic acid chloride. In this way, benzoyl chloride and its *o*- and *p*-chloro-, *o*- and *p*-bromo-, *p*-methoxy-, *m*- and *p*-nitro-, 3,5-dinitro-derivatives were formed as well as phenylacetyl chloride and cinnamyl chloride. The method is even more general than the one just described where the free organic acid is used; moreover, it is usually the method to be preferred as a smaller excess of oxalyl chloride may be used to get the maximum yields. This is due partly to the fact that less gas is evolved in the reaction so that less oxalyl chloride is lost by volatilization. The yields and the purity of the products are high. It is particularly noticeable that certain nitro derivatives of benzoic acid, which react with oxalyl chloride under the conditions described above to give double anhydrides, when allowed to react in the form of their sodium salts give exclusively acid chlorides.

Acid chlorides are also readily formed by the action of oxalyl chloride on acid anhydrides. This reaction is a smooth one and very good yields are obtained. In order to test out the scope of the reaction, the following anhydrides were converted into the corresponding acid chlorides: acetic, monochloroacetic, benzoic, *m*-nitrobenzoic, 3,5-dinitrobenzoic anhydrides. This reaction may be carried out merely by mixing oxalyl chloride with the acid anhydride alone or in the presence of benzene as a solvent and refluxing for a few hours. It is significant here that the anhydrides of the nitro derivatives of benzoic acid with oxalyl chloride readily change into the corresponding acid chlorides, whereas the double anhydrides of these same acids and oxalic acid are perfectly stable in the presence of oxalyl chloride.

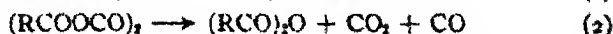
A description of the preparation of aromatic acid anhydrides¹ by the action of one mole of oxalyl chloride upon 2 moles of organic acid in benzene as a solvent has already been published.¹ The reaction apparently is general for this class of acids and the yields are very good. Again, certain nitro derivatives of benzoic acid act somewhat peculiarly, giving double anhydrides of oxalic acid which when melted decompose to give

¹ THIS JOURNAL, 40, 424 (1918).

the simple anhydrides. In this communication, the same procedure has been applied to the preparation of aliphatic acid anhydrides. In no case, however, are the yields so high as in the aromatic series. In most cases, certain amounts of unchanged acid and some acid chloride are obtained as by-products. The difference in yields of anhydrides with the aliphatic acids may probably be explained by the fact that the aliphatic acid anhydrides are easily converted into acid chlorides with oxalyl chloride whereas the aromatic acid anhydrides are less easily converted. The acids investigated were *n*-butyric, phenylacetic and cinnamic. The yields of acid anhydrides from aliphatic acids if no benzene is used as a solvent, are about the same as when a solvent is used.

Acid anhydrides may also be formed by the addition of one mole of oxalyl chloride to 2 or more moles of the sodium salt of the organic acids suspended in benzene. Under these conditions good yields of the aromatic acid anhydrides are obtained and in the aliphatic series, the yields are only slightly lower, the by-product of acid chloride being small. For the preparation of aliphatic acid anhydrides, the use of the sodium salts of the acids thus gives more satisfactory results than the free acids. The acids chosen for study were benzoic, *m*-nitrobenzoic, *p*-nitrobenzoic, *o*-chlorobenzoic, lauric, monochloroacetic, *n*-valeric and *n*-butyric. The most noticeable difference in the formation of the anhydrides from the sodium salts of the acids and from the free acids by the action of oxalyl chloride is in certain nitro derivatives of benzoic acid. These in the form of their sodium salts give simple anhydrides directly while as free acids, double anhydrides are produced.

The mechanism of the formation of these acid chlorides and acid anhydrides from oxalyl chloride and aliphatic and aromatic acids is cleared up by a consideration of the above reactions. There is no question but that the first step is the formation of a double anhydride, the second a decomposition of the double anhydride into a simple anhydride, and third, the conversion of the simple anhydride into the corresponding acid chloride as follows:



By the isolation of the intermediate double anhydrides in many cases it has been shown that the acid anhydrides form through these compounds. It was a question, however, whether the acid chlorides as produced from the acid and excess of oxalyl chloride actually form directly or through the acid anhydrides which are secondary products from the double anhydrides. This is clarified by the fact that the acids which form stable double anhydrides do not give acid chlorides with ---

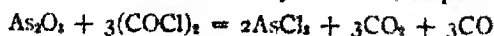
chloride but instead give double anhydrides. The acid chlorides certainly have an opportunity to form directly in these reactions since the acid dissolves in the excess of oxalyl chloride and the double anhydride does not begin to separate for some time after refluxing has started. The results signify that in certain cases the double anhydrides are so stable that they separate out without breaking down into the simple anhydride which would in turn yield the acid chloride. If any of the simple anhydrides, and especially to be noticed are the nitrobenzoic anhydrides, are treated with oxalyl chloride there is no difficulty in converting them practically quantitatively into the corresponding acid chlorides. The ease with which anhydrides form acid chlorides undoubtedly accounts for the presence of some acid chloride with the anhydrides, especially in the aliphatic series when 2 moles of acid are treated with one mole of oxalyl chloride.

Under ordinary conditions, it would be assumed that the mechanism of the formation of acid chlorides and acid anhydrides from the salts of the organic acids would be exactly analogous to the formation of the same compounds from the free organic acid. This probably is the case. Nevertheless, it is possible that the acid chlorides and anhydrides when formed from the sodium salts of the acids and oxalyl chlorides are not produced through the double anhydrides.



This assumption is made because of the fact that the sodium salts of certain nitro derivatives of the aromatic acids do not yield the double anhydrides when treated with oxalyl chloride but either acid chlorides or acid anhydrides, whereas the corresponding free acids invariably yield under any conditions the double anhydrides. It is difficult to explain why the salts of the acids and free acids act differently.

Since oxalyl chloride reacts so readily with organic acids and acid anhydrides, an attempt was made to prepare certain inorganic acid chlorides by the action of oxalyl chloride on the corresponding oxide. Two were chosen for study, arsenious oxide and chromium trioxide. In both cases, refluxing with a slight excess of oxalyl chloride causes a conversion of the oxides into arsenic chloride and chromyl chloride, respectively.



It is probable that this reaction could be extended to other oxides of the same sort.

Of the various reagents which may be used for the production of the Beckmann rearrangement in ketoximes, acid chlorides are by far the commonest. An attempt was made to use oxalyl chloride for this same

purpose. The results show that it is an excellent reagent for this purpose and causes very rapid and quantitative rearrangement of benzophenone oxime, phenylanisyl ketoxime and phenyltolyl ketoxime into the corresponding acid amides.

Oxalyl bromide may be formed by the action of hydrobromic acid upon oxalyl chloride.¹ This substance is extremely reactive and acts in an analogous manner to oxalyl chloride as shown by experiment. When 2 moles of an organic acid are treated in benzene with one mole of oxalyl bromide, acid anhydrides are produced; thus benzoic, *o*- and *p*-chloro- and *p*-bromobenzoic acids were converted into their anhydrides. The yields are good and the constants check with those obtained by the action of oxalyl chloride on the aromatic acids. The use of oxalyl bromide in this reaction, however, is of theoretical interest only since oxalyl bromide is formed from oxalyl chloride which is just as satisfactory for the preparation of acid anhydrides.

To show that acid bromides can be produced directly from oxalyl bromide and an organic acid, *n*-butyric acid was converted to butyryl bromide. The sodium salts of acids are also converted to acid bromides by means of oxalyl bromide, thus the sodium salts of benzoic acid and its *o*-, *m*- and *p*-chloro, *o*- and *p*-bromo, *p*-iodo-, *o*-, *m*- and *p*-methyl-, *p*-methoxy-, *m*- and *p*-nitro-, 3,5-dinitro derivatives as well as cinnamic and phenylacetic acids were converted to acid bromides. This particular method was extended to the large number of acids described above because it was noted in the literature that no aromatic acid bromides with the exception of benzoyl bromide had been described. These compounds could undoubtedly be produced by the action of oxalyl bromide directly on the organic acid, but since the reaction between the sodium salts of the acids and oxalyl bromide runs so smoothly and such a small excess of the oxalyl bromide is required, this method was adopted for their preparation.

Since the aromatic acid bromides have never been prepared up to the present time, it seemed desirable to determine whether the standard methods for the preparation of acid halides could be applied to these substances. Consequently the reaction between phosphorus pentabromide and certain aromatic acids and between phosphorus pentabromide and the sodium salts of certain acids was carried out. In every case acid bromides are obtained although not in such good yields or in such pure form as by the use of oxalyl bromide. The results indicate, nevertheless, that these general methods are applicable to the preparation of acid bromides.

Experimental.

Action of Oxalyl Chloride on Organic Acids—Preparation of Acid Chlorides.—The general procedure by which acid chlorides are pro-

¹ Ber., 46, 1432 (1913)

duced from acids by means of oxalyl chloride is as follows: In a round-bottom flask, the neck of which is ground to fit the bottom of a reflux condenser, is placed one mole of the organic acid and 2 to 2.5 moles of oxalyl chloride. In some cases, an evolution of gas starts immediately, indicating that the reaction is taking place; in other cases slight warming is necessary before gases are evolved. After once starting, the reaction proceeds spontaneously for 15-20 min. or sometimes even longer. After this period of time a small flame is again applied and the mixture refluxed for about 2 hours. The reaction mixture is then distilled under atmospheric pressure till the excess of oxalyl chloride is collected and then generally under diminished pressure (preferably in a flask such as is described by Noyes¹ without the separatory funnel attached, however) to obtain the acid chloride. By this method the series of acid chlorides which are given in the table below were produced.

Acid	Wt. of acid	Wt. of oxalyl chloride	Wt. of acid chloride	% Yield	B. p. or m. p. of acid chlorides	
					Deg.	Mm. Pressure
<i>n</i> -Valeric	25	77	28	95	107-110	756
Hydrocinnamic	35	60	38	98	116	15
Benzoic	25	60	28	98	93	20
<i>o</i> -Bromobenzoic	25	40	25	93	125	20
<i>p</i> -Bromobenzoic	10	15	10	94	181-2	125 (m. p. 42°)
Lauric	25	40	27	99	145-7	20
Salicylic	15	28	16.5	98		
Monochloroacetic	25	80	24	80	103-6	750
Phenylacetic	35	70	30	74	100	12

It is noticeable that only in 2 cases, namely monochloroacetic acid and phenylacetic acid, do the yields drop below 90%. Monochloroacetic acid forms an anhydride with extreme ease in the presence of almost any sort of dehydrating agent and small amounts were isolated in the above reaction. Phenylacetyl chloride is not very stable and extremely reactive, giving certain amounts of tarry material, probably condensation products between several molecules. The yields, however, in both cases, are very much better than are obtained with other acid chloride reagents with the possible exception of thionyl chloride.

The preparation of these acid chlorides can be carried out if desired in benzene as a solvent (about 50 cc. of benzene being used for a 25 g. portion of acid), thus, both benzoic and monochloroacetic acids gave satisfactory results under these conditions. In the case of salicylic acid, because of the instability of the acid chloride, the preparation of this latter compound was not attempted except with benzene as a solvent, and after the reaction had taken place the benzene and excess of oxalyl chloride were removed by distilling off under diminished pressure at room tem-

¹ THIS JOURNAL, 39, 2718 (1917)

perature. The action of oxalyl chloride upon *p*-hydroxybenzoic acid was carried out but complex condensation products were obtained and no acid chloride was produced.

When excess of oxalyl chloride reacts with *m* nitro, *p*-nitro-, 3,5-dinitro-, and 2,4,6-trinitrobenzoic acids, the acid at first goes into solution and in the course of a few minutes a solid separates. After refluxing for 2 hours, the reaction mixture is treated directly with benzene, the oil filtered, washed with dil. sodium carbonate solution (except in the case of the trinitrobenzoic acid), dried and washed with hot benzene. The benzene filtrates from the original reaction mixture are evaporated and a small amount of solid material is always obtained. This is unchanged acid. Of the 4 nitro compounds produced, the double anhydride of *m*-nitrobenzoic acid¹ and 3,5-dinitrobenzoic acid have already been described in a previous communication and the decomposition points here agree with those previously obtained. The double anhydrides of oxalic and *p*-nitrobenzoic acid as well as of 2,4,6-trinitrobenzoic acid, however, are new.

***p*-Nitrobenzoic Oxalic Anhydride, $(\text{NO}_2\text{C}_6\text{H}_4\text{COOCO})_2$.**—This substance forms yellowish crystals, melting with decomposition at 169–170° to form *p*-nitrobenzoic anhydride, white crystals from alcohol, m. p. 189–190°. The double anhydride decomposes immediately on treatment with pyridine.

Subs., 0.2159; 14.2 cc. N_2 at 25° and 750 mm.

Calc. for $\text{C}_{16}\text{H}_8(\text{NO}_2)_2$: N, 7.2. Found, 7.5.

2,4,6-Trinitrobenzoic Oxalic Anhydride, $[(\text{NO}_2)_3\text{C}_6\text{H}_2\text{COOCO}]_2$.—This substance forms slightly yellowish crystals which melt with decomposition at 228–230° to give 1,3,5-trinitrobenzene, m. p. 121°. The properties of this double anhydride from oxalic acid and trinitrobenzoic acid are slightly different from those of the other nitrobenzoic acids; first in that when melted it gives trinitrobenzene instead of trinitrobenzoic anhydride as would be expected, and second, that it readily decomposes with sodium carbonate solution to give the sodium salt of trinitrobenzoic acid. Similar to the other nitro double anhydrides, it decomposes rapidly with pyridine.

Subs., 0.1395; 18.9 cc. N_2 at 27° and 748 mm.

Calc. for $\text{C}_{12}\text{H}_2\text{O}_8\text{N}_6$: N, 14.8. Found, 15.2.

Action of Oxalyl Chloride on the Sodium Salts of Organic Acids—Preparation of acid Chlorides.—The general procedure by which acid chlorides are produced from the sodium salts of acids and oxalyl chloride is as follows. A round-bottom flask is used which has 2 openings; the one is a neck ground to fit a reflux condenser and the second is a side tube (1.5 cm. in diameter and 2.5 cm. long). This second side tube is cork-

¹ THIS JOURNAL, 40, 424 (1918).

stoppered and is used for the addition of solid sodium salt. In the flask with the reflux condenser attached is placed 1.2 to 1.5 moles of oxalyl chloride dissolved in benzene (20 cc. of benzene is used when about 10 g. of oxalyl chloride is needed). One mole of the dry sodium salt of the acid is now added in small portions through the side arm. Upon each addition, gases are evolved. After all of the sodium salt has been added, the mixture is refluxed for 2 hours with occasional stirring to be certain that the reaction is completed. At the end of this time the sodium chloride and any traces of unchanged sodium salt of the organic acid are filtered off. The filtrate is distilled and after recovering the benzene, the acid chloride, if solid, is crystallized or if a liquid, vacuum distilled. In this way yields of acid chloride varying from 75% to over 90% are easily produced. In the experiments carried out to test the method only small amounts (10 to 20 g.) of the sodium salts of the acid were used and consequently the loss involved in a distillation or crystallization was proportionately large. It is probable that if 100 g. lots of acid chloride should be made, the yields would be consistently over 90%. The compounds are practically pure as obtained directly from the benzene, but in the experiments described the products were either recrystallized or once distilled. By this method, the following acid chlorides were made: cinnamyl, phenylacetyl, benzoyl, and the following substituted benzoyl chlorides: *p*-chloro-, *o* bromo-, *p* bromo-, *p*-methoxy-, *m*-nitro-, *p* nitro-, and 3,5-dinitro-. The constants agreed in every case with those appearing in the literature.

Action of Oxalyl Chloride on Organic Acid Anhydrides—Preparation of Acid Chlorides.—The general procedure by which acid chlorides are produced from acid anhydrides by means of oxalyl chloride is as follows. In a round-bottom flask of the type used for the production of acid chlorides from organic acids and oxalyl chloride, is placed one mole of the organic acid anhydride and 1.5 to 2.5 moles of oxalyl chloride. The mixture is gently refluxed for 2 hours. Evolution of gas takes place, as the reaction proceeds. At the end of the heating, the reaction mixture is distilled to free it from the excess of oxalyl chloride and the acid chloride which is thus obtained is purified by crystallization or distillation under atmospheric pressure or diminished pressure. By this general process, acetic, monochloroacetic, benzoic, *m* nitro- and 3,5-dinitro benzoic acid anhydrides were converted into the corresponding acid chlorides, and yields of 80-95% obtained.

The Action of Oxalyl Chloride on Organic Acids—Preparation of Organic Acid Anhydrides.—The general procedure by which acid anhydrides are produced from acids and oxalyl chloride is as follows. A benzene solution or suspension is made of 2 moles of aromatic acid (100 cc. of benzene for 25 g. of organic acid) and one mole of oxalyl chloride

is gradually run in. The mixture is refluxed for 2 hours and then the benzene distilled off. The yields of aromatic acid anhydrides¹ by this method are very good, but in the aliphatic series they seldom amount to more than 50% to 70%. As by-products in these latter reactions are obtained free acid and acid chloride. The particular compounds which were studied were *n*-butyric acid (56% yield), phenylacetic acid (46% yield) and cinnamic acid (76% yield). If these same reactions with the acids are carried out without benzene as a solvent, the yields are about the same as indicated.

The Action of Oxalyl Chloride on the Salts of Organic Acids—Preparation of Organic Acid Anhydrides.—The general procedure is to suspend 2 moles of the powdered, dry sodium salt of the acid in benzene (50 cc. of benzene for 25 g. of sodium salt) and then to allow 1 to 1.2 moles of oxalyl chloride to run in. The reaction takes place rapidly and after 2 hours refluxing, is complete. The sodium chloride is filtered off and the anhydrides are obtained by evaporation of the benzene. With some of the aromatic acids, the anhydrides are only slightly soluble in benzene and consequently must be recovered from the mixture with sodium chloride by treatment with dilute sodium carbonate. The aromatic acid anhydrides as obtained from the benzene are washed with dil. sodium carbonate solution, dried and recrystallized while the aliphatic acid anhydrides are purified by distillation with a good fractionating column. In the aromatic series, the yields are very good, amounting to 75% to 90%. In the aliphatic series, however, some acid chloride is produced although in smaller amounts than when anhydrides are made from the free acids and oxalyl chloride. The sodium salts of the following acids were converted to anhydrides as just described: benzoic, *m*- and *p*-nitrobenzoic, *o*-chlorobenzoic, monochloroacetic (54% yield), *n*-butyric (79% yield), *n*-valeric (91% yield), lauric (80% yield). The physical constants were not different from those already given in the literature.

Action of Oxalyl Chloride on Inorganic Acids—Preparation of Inorganic Acid Chlorides.—In a flask similar to the one used in the previous experiments are placed arsenic trioxide (one mole) and excess of oxalyl chloride (2 moles). The reaction mixture is refluxed gently for 5 hours, during which time the oxide gradually goes into solution. The reaction mixture is then distilled, a small excess of oxalyl chloride collected first and then the arsenic trichloride, b. p. 130°. The yield amounts to about 95%.

In the same way dry chromium trioxide (one mole) and oxalyl chloride (2 moles) upon refluxing for 5 hours gives an 80% yield of chromyl chloride, b. p. 114°–116° at 748 mm.

¹ *Loc. cit.*

Action of Oxalyl Chloride on Certain Aromatic Ketoximes—Preparation of Substituted Acid Amides.—Benzophenone oxime, anisyl-phenyl ketoxime and phenyl-*p*-tolyl ketoxime are treated in the following way: One mole of the ketoxime is dissolved in a small amount of absolute ether. To the solution is added slowly $\frac{3}{4}$ of a mole of oxalyl chloride. The mixture is kept warm for 10 minutes, during which time acid amide separates. At the end of this period half of the ether is evaporated, the mixture cooled and the solid acid amide filtered. The yields of benzanilide, anisanilide and *p*-toluic anilide amount to over 90%.

Action of Oxalyl Bromide on the Sodium Salts of Organic Acids—Preparation of Acid Bromides.—The general procedure by which acid bromides are produced from the sodium salts of the acids is exactly analogous to the method used for the preparation of acid chlorides from the sodium salts of organic acids and oxalyl chloride. The products are worked up in exactly the same way. The yields of acid bromides are in general over 90%. The following table contains a list of the bromides thus prepared with their constants and chemical analyses.

Benzoyl bromide, C_6H_5COBr B p 218–220° at 739 mm as compared with 218–219° reported in the literature¹

o-Chlorobenzoyl bromide, ClC_6H_4COBr B p 143–145° at 37 mm

Subs., 0.2436, $AgCl + AgBr$, 0.3372

Calc. for C_7H_4OBrCl $AgCl + AgBr$, 0.3392

m-Chlorobenzoyl bromide, ClC_6H_4COBr B p 143–147° at 40 mm

Subs., 0.2580, $AgCl + AgBr$, 0.3860

Calc. for C_7H_4OBrCl : $AgCl + AgBr$, 0.3894

p-Chlorobenzoyl bromide, ClC_6H_4COBr B p 141–143° at 27 mm

Subs., 0.2750; $AgCl + AgBr$, 0.4180

Calc. for C_7H_4OBrCl . $AgCl + AgBr$, 0.4150.

o-Bromobenzoyl bromide, BrC_6H_4COBr B p 166–168° at 18 mm

Subs., 0.2420; $AgBr$, 0.3464.

Calc. for $C_7H_4OBr_2$: Br , 60.6. Found 60.9.

p-Bromobenzoyl bromide, BrC_6H_4COBr B p 135–137° at 18 mm.

Subs., 0.1600, $AgBr$, 0.2290.

Calc. for $C_7H_4OBr_2$: Br , 60.6. Found 60.8.

p-Iodobenzoyl bromide, IC_6H_4COBr . White crystals from carbon tetrachloride m. p. 54–55° Within 2 days it turns very dark colored even though in a sealed tube.

Subs., 0.1850; $AgBr + AgI$, 0.2460

Calc. for C_7H_3OBrI : $AgBr + AgI$, 0.2490.

o-Methylbenzoyl bromide, $CH_3C_6H_4COBr$ B. p 133–136° at 37 mm.

Subs., 0.2180; $AgBr$, 0.2080.

Calc. for C_8H_7OBr . Br , 40.2. Found: 40.5.

m-Methylbenzoyl bromide, $CH_3C_6H_4COBr$ B. p. 136–137° at 32 mm.

Subs., 0.2350, $AgBr$, 0.2310.

Calc. for C_8H_7OBr . Br , 40.2 Found: 40.1.

¹ *Ber.*, 14, 2473 (1881).

p-Methylbenzoyl bromide, $\text{CH}_3\text{C}_6\text{H}_4\text{COBr}$. B. p. 145–149° at 42 mm.

Subs., 0.2806; AgBr, 0.2630.

Calc. for $\text{C}_7\text{H}_7\text{OBr}$: Br, 40.2. Found: 40.0.

p-Methoxybenzoyl bromide, $\text{CH}_3\text{OC}_6\text{H}_4\text{COBr}$. B. p. 183–186° at 27 mm.

Subs., 0.2310; AgBr, 0.2058

Calc. for $\text{C}_8\text{H}_7\text{O}_2\text{Br}$: Br, 37.3. Found: 37.6.

m-Nitrobenzoyl bromide, $\text{NO}_2\text{C}_6\text{H}_4\text{COBr}$. B. p. 165–167° at 18 mm. The compound is a yellowish solid at room temperature and may be crystallized from carbon tetrachloride, m. p. 42–43°.

Subs., 0.1590; AgBr, 0.1315.

Calc. for $\text{C}_7\text{H}_5\text{O}_2\text{NBr}$: Br, 34.8. Found: 35.1.

p-Nitrobenzoyl bromide, $\text{NO}_2\text{C}_6\text{H}_4\text{COBr}$. Yellow crystals from carbon tetrachloride, m. p. 63–64°.

Subs., 0.2456; AgBr, 0.2048.

Calc. for $\text{C}_7\text{H}_5\text{O}_2\text{NBr}$: Br, 34.8. Found: 35.0.

3,5-Dinitrobenzoyl bromide, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{COBr}$. Yellow crystals from carbon tetrachloride, m. p. 59–60°.

Subs., 0.2120; AgBr, 0.1474.

Calc. for $\text{C}_7\text{H}_3\text{O}_4\text{N}_2\text{Br}$: Br, 29.3. Found: 29.6.

Cinnamyl bromide, $\text{C}_6\text{H}_5\text{CH}=\text{CHCOBr}$. B. p. 180–184° at 40 mm. This compound forms yellow crystals, m. p. 47–48°.

Subs., 0.2749; AgBr, 0.2448.

Calc. for $\text{C}_9\text{H}_9\text{OBr}$: Br, 37.9. Found: 38.0.

Phenylacetyl bromide, $\text{C}_6\text{H}_5\text{CH}_2\text{COBr}$. B. p. 150–155° at 50 mm.

Subs., 0.2642; AgBr, 0.2505.

Calc. for $\text{C}_8\text{H}_9\text{OBr}$: Br, 40.1. Found: 40.4.

Other Reactions with Oxalyl Bromide.—In order to determine whether oxalyl bromide might be used in place of oxalyl chloride for the production of acid anhydrides, benzoic acid, *o*- and *p*-chloro- and *p*-bromobenzoic acids were treated in benzene in the proportion of 2 moles of acid to one mole of oxalyl bromide. The directions followed were exactly analogous to those used with oxalyl chloride and in every case very good yields of the corresponding anhydrides were produced.

In order to show that excess of oxalyl bromide on the organic acids will yield acid bromides in the same way that oxalyl chloride yields acid chlorides, *n*-butyric acid (one mole) was refluxed with an excess of oxalyl bromide (2 moles) as described under the reaction between organic acids and oxalyl chloride. After the evolution of gas stopped, the reaction mixture was refluxed for 2 hours and then distilled in the usual way. The bromide was produced in good yields.

The Action of Phosphorus Pentabromide upon Aromatic Acids and the Salts of Aromatic Acids.—One mole of phosphorus pentabromide is suspended in benzene and one mole of organic acid is added. The mixture is refluxed for 1 to 2 hours, at the end of which time the reaction is complete. Upon distillation under diminished pressure, phosphorus oxybromide comes over first and then the acid bromide. In this way benzoic

and *o*-chlorobenzoic acids were converted to the acid bromides. The yields amounted to about 50%. The constants were the same as those already mentioned.

If the phosphorus pentabromide is suspended in benzene (50 cc. of benzene to 25 g. of acid) and the dry sodium salt of the acid is added gradually, a rapid reaction takes place and after refluxing a short time is complete. The sodium bromide is filtered off and the benzene filtrate distilled, first under atmospheric pressure to remove the benzene, then under diminished pressure to remove the phosphorus oxybromide and finally the acid bromide. The yields of pure product amount to 60-75%. By this method benzoic acid and its *o*- and *p*-bromo-, *o*- and *m*-methyl-, *m*-nitro-, 3,5-dinitro derivatives were converted into the corresponding acid bromides.

Summary.

1. Organic acids when treated with 2 moles of oxalyl chloride alone or in benzene as a solvent are converted almost quantitatively into acid chlorides.
2. The sodium salts of organic acids when added to 1.2-1.5 moles of oxalyl chloride in benzene are converted almost quantitatively into acid chlorides.
3. Certain nitro derivatives of benzoic acid when treated as in (1) are converted into double anhydrides of oxalic acid and the aromatic acid, when treated as in (2) are converted into acid chlorides as is the case with other acids.
4. Organic acid anhydrides when treated with oxalyl chloride are converted almost quantitatively into acid chlorides.
5. Certain inorganic oxides are readily converted by oxalyl chloride into the corresponding acid chlorides.
6. Aromatic organic acids (2 moles) when treated in benzene solution with oxalyl chloride (one mole) are converted almost quantitatively into acid anhydrides. Aliphatic organic acids under the same treatment are converted to acid anhydrides only to the extent of 50-70%, some unchanged acid and acid chloride being by-products.
7. The sodium salts of aromatic organic acids (2 moles) when suspended in benzene and treated with oxalyl chloride (one mole) are converted almost quantitatively into acid anhydrides. In the aliphatic series, the yields of acid anhydride are not so good as in the aromatic series, but much better than are obtained by the action of oxalyl chloride on the free organic acid.
8. Certain nitro derivatives of benzoic acid when treated as in (6) are converted into double anhydrides of oxalic acid and aromatic acid; when treated as in (7) are converted into acid anhydrides as is the case with other acids.

9. The Beckmann rearrangement in ketoximes is readily produced by the action of oxalyl chloride.

10. If organic acids or the salts of organic acids are treated with oxalyl bromide under the same conditions as in (1), organic acid bromides are produced. Several new aromatic acid bromides are described.

11. Organic acids are converted into their anhydrides by oxalyl bromide when treated as described in (6).

12. Organic acids or the sodium salts of organic acids are converted into acid bromides by the action of phosphorus pentabromide.

13. The mechanism of the reaction of oxalyl chloride with organic acids and their sodium salts is described.

URBANA, ILL.

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION]

A MODIFICATION OF THE APPARATUS FOR THE DETERMINATION OF ARGININE NITROGEN BY VAN SLYKE'S METHOD.

BY GEORGE F. HOLM

Received January 10, 1920

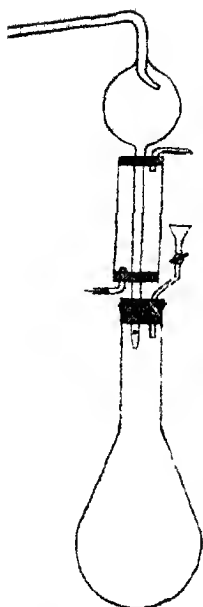
Difficulty is sometimes encountered by beginners, and even by experienced investigators at times, in the determination of arginine nitrogen of a protein hydrolysate by Van Slyke's method.¹ Even with extreme care, the use of boiling tubes, pumice, etc., cannot always prevent bumping, with the result that quite often a portion of the standard acid contained in the Folin bulb will be ejected by a sudden evolution of steam.

It has also been observed that even after cooling thoroughly upon completion of the digestion of the solution with 50% potassium hydroxide solution, a moistened strip of red litmus paper inserted into the neck of the flask will slowly turn blue (indicating ammonia). This in turn may result in a slight loss of ammonia upon the transfer of the flask to a Kjeldahl distillation rack as is required in this method of procedure given by Van Slyke. We have devised a modified apparatus which eliminates these difficulties. The apparatus requires no technique in glass blowing or new material not already on hand in a chemical laboratory.

A straight piece of glass tubing 10 cm. in length and of 3.3 cm. diameter is fitted to a Kjeldahl trap with 2 rubber stoppers as shown in the diagram. Into these rubber stoppers have previously been inserted an inlet and an outlet tube for water. This serves as a condenser for vapors during the 6 hours of digestion.

To make the apparatus suitable for an ordinary Kjeldahl rack, the neck of a Kjeldahl flask is cut off to a length of about 10 cm. In order to add the 100-200 cc. of water before the final distillation of ammonia, without

¹ D. D. Van Slyke, *J. Biol. Chem.*, 10, 25-33 (1911).



opening the system, a separatory funnel is inserted in the stopper. In using this apparatus 12.5 grams of potassium hydroxide and a few pieces of pumice stone are placed in the Kjeldahl flask. Twenty-five cc. of the "bases" is then added and the apparatus fitted upon a Kjeldahl distillation rack with a receiver containing 0.0714 *N* standard acid, as in an ordinary Kjeldahl determination (bringing exit of tube as near the surface of the standard acid as possible). During the 6 hours' digestion with potassium hydroxide a stream of water is directed through the condenser. The condenser is then drained and the system allowed to cool. From 100 to 200 cc. of water is then added through the separatory funnel, together with a small amount of zinc dust. The final distillation is now conducted as in a regular Kjeldahl determination until 100-200 cc (depending on the volume of water added) of distillate has been collected.

The titration and calculation of the "arginine" nitrogen are carried out in the usual manner.

The advantages of this apparatus over that described by Van Slyke have already been given

- (a) There is no danger of loss due to "bumping."
- (b) No break in the system or transfer of material is necessary.
- (c) The rather expensive "Folin bulb" is eliminated

ST PAUL, MINN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE KENTUCKY AGRICULTURAL EXPERIMENT STATION]

THE SIGNIFICANCE OF THE PEROXIDASE REACTION WITH REFERENCE TO THE VIABILITY OF SEEDS.

By J. S. McHARGUE

Received January 19, 1920

Among the various enzymes that occur in living animal and vegetable tissue perhaps none is more vital to the life process than those concerned with oxidation within the cells. This oxidation is brought about by the oxidases and the peroxidases which are widely disseminated through the living tissues of both animals and plants. During the life and growth of plants oxidases are abundant in all the tissues; however, when maturity is reached, peroxidases predominate in the seeds of most species of plants. A few species contain both oxidases and peroxidases. Sound, well-matured, fresh seeds of all the species thus far examined have shown a pronounced

peroxidase reaction after having been crushed and finely ground in the presence of air.

Kastle,¹ in his memoir on the oxidases, states that the peroxidases and catalases seem to be even more widely distributed in various living tissues of the plant and animal than the oxidases. He further states that to such an extent is this the case that the properties of these substances might almost be turned to account as a general chemical test for vital activity. He also states that it can certainly be said of any tissue or organ that it is dead when it fails to show the reactions of the peroxidases and catalases. However, the writer has recently observed certain specimens of dead grains in which little or no peroxidase reaction could be obtained, yet they contained a substance which decomposed hydrogen peroxide, thus showing the presence of a catalase in the absence of a peroxidase. This observation, therefore, indicates that the peroxidase reaction may be a specific test for viability of seeds, although catalase activity may not be.

Brocq-Rosseau and Gain² have tested for peroxidases in samples of wheat varying in age from 2 years to 5000 years. They state that all viable seeds tested showed the peroxidase reaction. They report finding peroxidases in a sample of wheat 2000 years old and came to the conclusion that peroxidases existed in the wheat a hundred years after it had lost the power to germinate. The latter statement appears quite remarkable since the writer has obtained seeds of several different species of plants, which showed zero germination and did not give a peroxidase reaction. In every case where the seeds have shown a weak or zero germination by methods in use in seed-testing laboratories, it has been found that another portion of the same lot of seeds showed a weak or zero peroxidase reaction, thus showing a close parallelism between the germination and the peroxidase test. Seeds showing zero germination, which gave no peroxidase reaction when tested with guaiacum solution and hydrogen peroxide are corn, hemp seed, tomato seed, tobacco seed, oats, cowpeas, soy beans, castor beans and two samples of lettuce seed.

The peroxidase test has been applied to a considerable number of seeds of different species of plants upon which no germination test has as yet been made, but from all external appearances the germination test would run 90%, or above, and in every case where sound seeds were ground in air a deep blue color has been obtained.

In order to determine the relative proportions of the peroxidase enzyme in the germ and the endosperm, the germs were dissected from

¹ J. H. Kastle, "The Oxidases and Other Oxygen-Catalysts Concerned in Biological Oxidations," *U. S. Public Health Ser Hyg. Lab. Bull.* 59.

² Brocq-Rosseau and Gain, "Sur la durée des peroxydases des grains," *Compt. rend.*, 146, 545-548 (1908)

Several grains of sound corn and the two different portions ground separately in a clean porcelain mortar and each part tested for peroxidases. The germs gave a deep blue color, whereas the endosperm gave only traces of blue coloration, thus showing that the substance which gives the peroxidase reactions is contained in the germ.

In another experiment, sound grains of corn were immersed in strong alcohol in a shallow vessel and the germs removed and ground beneath the surface of the alcohol. The alcohol was then diluted with 3 volumes of distilled water and the peroxidase reagents added. Only a pale blue color was obtained, thus showing either that the enzyme substance had been destroyed by the strong alcohol or that oxygen had been excluded to such an extent that but little peroxidase was formed under these conditions. The germs from other grains of corn of the same sample were dissected from the endosperm and ground, beneath the surface of distilled water, and tested for peroxidases in the usual way. A depth of color somewhat comparable with that obtained when the germs were removed under alcohol, was obtained, thus showing that the germs of grains of corn contain a substance which, on exposure to oxygen, absorbs the latter rapidly and a peroxidase is formed in this process.

It is interesting to note that among the 20 or more different species of seeds which have been tested, only 3 have contained both oxydases and peroxidases. Soy beans gave a pronounced oxidase and a peroxidase reaction. Alfalfa seed showed a weak oxidase reaction and a strong peroxidase reaction. Lettuce seed gave an intense oxidase and a moderate peroxidase reaction. Lettuce seed that showed zero germination gave an oxidase reaction of equal intensity to that given by seeds which showed a high percentage of germination. However, upon destroying the oxidase reaction by carefully heating until the blue color was destroyed, cooling to room temperature and adding hydrogen peroxide, no peroxidase reaction was obtained upon the seed that showed zero germination, whereas the sound seed showed a strong peroxidase reaction after this treatment, thus showing that the peroxidase reaction was quite specific as a test for seed viability, in this particular case.

On applying the test for peroxidases to 3 different samples of oats which had a germination of 80, 44 and 0%, respectively, a deep blue color was obtained with the sample showing 80% germination; a decidedly lighter blue color was obtained with that showing 44% germination and only a light blue was obtained with the sample showing zero germination, thus showing a close and unmistakable agreement between the germination test and the peroxidase reaction. The temperature at which the blue color was destroyed increased with the viability of the seeds. The light blue color or the zero viability was destroyed between 60-65, the 44% viability at 65-70 and the 80% between 70-75°. Experiments

are under way with known mixtures of viable and non-viable seeds for the purpose of establishing a color scale from which the approximate percentage of germination of a given sample of seed may be estimated by means of the peroxidase test.

Tests on the temperature at which the oxidase and the peroxidase reactions are destroyed show some variation with different species of seeds.

Conclusions.

1. From the results obtained, the writer is convinced that the peroxidase reaction can be made use of in seed-testing laboratories for detecting non-viable seed and for distinguishing between seed of high, medium and low viability.
2. That lettuce, alfalfa and soy-bean seeds are unique in that they contain both oxidases and peroxidases.
3. That the vital property of seeds is contained in a substance (presumably an oxygenase) which has the power to activate molecular oxygen, when exposed to the air, peroxidases being formed, and that when this power is lost the seed loses its power to germinate.
4. That the peroxidase reaction may be further turned to account in determining the rate at which seeds lose their viability.

LEXINGTON, KY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF POMONA COLLEGE AND
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THE IDENTIFICATION OF PHENOLS. II.

BY JAMES A. LYMAN¹ AND E. EMMET REID.

Received January 21, 1920

In a former article² it was shown that *p*-nitrobenzyl bromide reacts readily with alkaline solutions of phenols to give well characterized ethers which may be used for the identification of the phenols. It was thought desirable to extend this work to other phenols.

Materials and Methods.

The *p*-nitrobenzyl chloride was made by nitrating benzyl chloride and separating the *para* compound by crystallization. The *p*-nitrobenzyl bromide was made by brominating *p*-nitrotoluene.

Into a 100 cc. flask was measured 25 cc. of 0.2 *N* sodium alcoholate and a nearly equivalent amount of the phenol. Except in the case of the salicylic acid esters the mixture was left slightly alkaline to avoid contamination of the product with the phenol. The reagent, usually 1.0 g. in amount, was added and the solution heated one hour under a

¹ The experimental work except that on salicylic acid esters was done at Pomona College by J. A. L.

² THIS JOURNAL, 39, 304 (1917).

JAMES A. LYMAN AND E. EMMET REID.

TABLE I.

	Solvent.		First crop.		Second crop.	
	Vol.	%.	Wt.	M. P. °C.	Wt.	M. P. °C.
<i>o</i> -Nitrophenol, 1 g. chloride	32	75	0.87	123	0.33	71
	40	58	0.67	130
	37	73	0.66	130	0.02	127
<i>p</i> -Nitrophenol, 1 g. chloride . . .	30	80	0.81	70-165	0.35	70
	65	84	0.57	165	emul.	...
	0.54	187.7	emul.	...
	0.51	187.4	emul.	...
2,4-Dinitrophenol, 0.8 g. chloride..	45	53	0.45	68-241	0.25	68
	50	95	0.04	248	0.28	72
<i>o</i> -Chlorophenol, 1 g. bromide . . .	37	63	1.20	97.5	0.07	83
	19	80	1.16	99	0.03	83
	1.14	99.4	trace	..
	1.06	100.1	trace	...
	1.00	100	trace	...
<i>p</i> -Chlorophenol, 1 g. bromide . .	37	63	1.19	101.5
	19	80	1.14	101.5	0.02	101.5
	1.12	101.3
3-Tribromophenol, 0.5 g. bromide	25	95	0.44	163.5	emul.	...
	70	81	0.41	163.5	trace	...
Gemicol, 1 g. chloride.	25	95	1.08	63	emul.	...
	35	66	0.99	63.6	emul.	..
	35	66	0.87	63.6	emul.	...
α -Naphthol, 0.8 g. chloride	30	80	0.84	133	emul.	...
	45	84	0.63	140	emul.	...
	60	79	0.61	140	emul.	...
β -Naphthol, 0.8 g. chloride..	33	83	0.68	106.7	emul.	...
	49	70	0.68	106.5	emul.	...
Salol, 1 g. bromide	30	80	0.90	77	emul.	...
	20	74	0.63	80.5	0.15	69
	14	68	0.55	84	0.04	74
	19	66	0.42	86	0.03	69
	15	63	0.36	87	0.03	69
	15	63	0.31	87	0.02	85
<i>p</i> -Cresyl salicylate, 1 g. bromide. .	25	95	0.89	128	oil	...
	27	95	0.68	139.5	emul.	...
	40	72	0.63	142.5
	40	72	0.61	142.5	emul.	...
<i>m</i> -Cresyl salicylate, 1 g. bromide. .	40	72	0.81	oil	emul.	...
	19	80	0.39	95-100	emul.	...
	14	70	0.29	115	emul.	...
	0.27	118	emul.	...
	0.36	118	emul.	...

reflux condenser after which more or less water was added, the amount being judged by the readiness of the product to separate out on cooling. The crystals filtered off were called "First Crop" and those obtained by adding a large volume of water "Second Crop." The first crop was recrystallized till the melting point became constant.

Results.

The results are given in tabular form, the first line representing the original preparation and succeeding lines the recrystallizations of the product. Under "Solvent" are given the volume and strength of the alcohol from which the crystals were obtained.

Picric acid, carvacrol, *m*-aminophenol and *p*-cresyl salicylate were tried but did not give satisfactory results.

Salicylic Acid Esters.

It has been shown by many chemists¹ that when an ester of one alcohol is dissolved in another alcohol, the second alcohol replaces the first, till equilibrium is reached. Normally this reaction is extremely slow but becomes enormously rapid in the presence of sodium alcoholate, as has been shown by many investigators. An example of this has been given by Reid.² From the work of Anderson and Pierce³ phenyl acetate does not seem to undergo this reaction, or at least not rapidly. The results given above with salol and with the *ortho* and *meta* cresyl salicylates agree with this, showing as they do, that the ethyl alcohol used as solvent did not replace the phenol or cresols in the salicylates, even when excess alkali was present.

p-Nitrobenzyl derivatives were prepared from methyl salicylate exactly as above, using a slight excess of sodium ethyl alcoholate and crystalline derivatives were readily obtained in excellent yields and worked up as usual. The one from methyl salicylate melted, crude, at 119° and, on recrystallization, at 123.8° and 124°. That from ethyl salicylate melted, crude, at 123.5° and, on recrystallization at 124.5° and 124.5°, showing it to be very pure from the start, while the derivative prepared starting with the methyl ester melted low at first. The practical identity of the melting points suggested that the methyl salicylate had been almost entirely transformed into the ethyl ester and that both products were the *p*-nitrobenzoyl derivative of ethyl salicylate, $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}-\text{C}_6\text{H}_4\text{COOC}_2\text{H}_5$. This appeared to offer an interesting case of ester transformation and these derivatives were further studied from that point of view. The derivatives of these esters and of *n*-butyl salicylate

¹ For a number of references and further discussions see Pardee and Reid, *J. Ind. Eng. Chem.*, 12, 129 (1920).

² *Am. Chem. J.*, 45, 506 (1911).

³ *J. Phys. Chem.*, 22, 49 (1918).

were prepared, using the corresponding alcohol as solvent in each case. The reagent was 1.0 g. of bromide in all of the preparations that follow.

TABLE II.

	Solvent.		First crop.		Second crop.	
	Vol.	%.	Wt.	M. P. °C.	Wt.	M. P. °C.
Methyl salicylate in MeOH.....	30	83	1.05	128.2	oil	...
	35	100	0.89	128.2	0.11	127.5
Ethyl salicylate in EtOH.....	30	80	1.02	122-3	emul.	...
	18	87	0.93	124.2	0.06	95-8
	15	95	0.84	125	0.07	110
Butyl salicylate in BuOH.....	15	..	1.12	90.3	oil	..
	15	95	1.02	91-2	0.05	86.7
	15	MeOH	0.78	91-2	0.15	89
	18	85	0.68	92	0.06	90

In the last case, the first and third recrystallizations were from ethyl and the second from methyl alcohol.

In the next two preparations methyl and butyl salicylates were used in ethyl alcohol solution, taking care, however, to use an excess of ester over alkali. The results show that the butyl derivative was obtained pure, but with some difficulty, while the methyl could never be gotten up to the proper melting point. Slight ester transformation must have taken place in both cases, which was to be expected, since slight alcoholysis of the phenolates would take place. The details are given in Table III.

TABLE III.

	Solvent.		First crop.		Second crop.	
	Vol.	%.	Wt.	M. P. °C.	Wt.	M. P. °C.
Methyl salicylate in EtOH.....	35	70	1.06	122	liq.	...
	20	MeOH	0.85	125	0.13	111
	30	MeOH	0.71	126.5	0.11	118
	25	MeOH	0.61	126.5	0.07	123
	10	BuOH	0.34	126.5	0.08	90
Butyl salicylate in EtOH.....	25	75	1.22	86-9	emul.	...
	20	72	1.12	86-90	0.06	78
	25	MeOH	0.67	92	0.23	78
	13	EtOH	0.43	92	0.01	85

It appears that the transformation of the esters is minimized by using excess of the salicylic ester and that characteristic derivatives can be obtained, though not in very pure form.

In the case of the methyl salicylate derivative above, the attempt was made to change the methyl into the butyl derivative by adding a small amount of sodium to the butyl alcohol from which the last crystallization was made. The solution took on a purple color on addition of the compound to the sodium butylate solution. As shown by the melting point of the crystals that were obtained from this solution, no such reaction had taken place. The most probable explanation is that the de-

rivative is a strong enough acid to remove practically all of the sodium butyrate from solution. An examination of the formula



shows the presence of the $-\text{CH}_2-$ group between two strongly negative groups. The nitro group may be concerned in the salt formation. Several other experiments of this kind were tried and all agreed with this in showing that these derivatives when once formed are not readily transformed by alcoholysis.

To show the effect of alcoholysis, or ester transformation, the following 3 experiments were tried. The salicylic acid esters were measured accurately into the alcohols in which 10% of sodium over that equivalent to the esters had been dissolved. These solutions stood for a time and were then heated, each with one g. of the reagent. The results are given below in the usual form.

TABLE IV.

	Solvent		First crop		Second crop	
	Vol.	%	Wt.	M. p.	Wt.	M. p.
Methyl salicylate in BuOH	20	72	0.15	91	0.27	88
	8	60	0.12	91	0.01	86
Ethyl salicylate in MeOH	30	84	0.74	127.5	0.02	124
	15	EtOH	0.68	127.5	0.02	126
Butyl salicylate in MeOH	30	84	0.56	127	0.05	118
	13	EtOH	0.50	127.3	0.02	125

It appears, in every case, that the derivative obtained corresponds to the alcohol that is used as solvent and not to that originally present in the ester. The products obtained melted slightly low but close enough to the true melting point to be sure that the transformations had been practically complete.

Summary.

It has been found that *p*-nitrobenzyl esters may be used to identify salicylic esters provided no excess alkali is present. They are best made in the alcohol corresponding to the ester.

p-Nitrobenzyl ethers have been made of the following phenols and these properties studied:

<i>o</i> -Nitrophenol, m. p. 130°.	α -Naphthol, m. p. 140°.
<i>p</i> -Nitrophenol, m. p. 187.4°.	β -Naphthol, m. p. 106.5°.
2,4-Dinitrophenol, m. p. 248°.	Salol, m. p. 87°.
<i>o</i> -Chlorophenol, m. p. 100°.	Methyl salicylate, m. p. 128.2°.
<i>p</i> -Chlorophenol, m. p. 101.3°.	Ethyl salicylate, m. p. 125°.
2,4,6-Tribromophenol, m. p. 163.5°.	Butyl salicylate, m. p. 92°.
Guaiacol, m. p. 63.6°.	<i>o</i> -Cresyl salicylate, m. p. 142.5°.
<i>m</i> -Cresyl salicylate, m. p. 118°.	

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE NORTHWESTERN UNIVERSITY MEDICAL SCHOOL.]

THE LIPOLYTIC ACTIVITY OF THE CASTOR AND SOY BEAN.

BY ARTHUR WILLIS BARTON

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Since 1900 there have been many investigations of the behavior of animal and vegetable lipases. These investigations have had a number of objects in view, such as the determination of the effect upon the lipase enzyme of media containing various salts,¹ alkalies,² acids,^{3,4,5,6} and preservatives,⁷ and the relation of lipase to a variety of substrates, including natural fats,^{8,9,10,11,12} ethyl butyrate,¹³ ethyl acetate,¹⁴ and amyl salicylate.¹⁵ But there has been so much variation in the mode of attack used by different investigators that it is difficult to make comparisons between their results.

The present work was planned to determine a few of the properties of the lipases of the castor and soy bean. The effect of increasing concentrations of acidity from the neutral point on the activity of the lipases was determined. The amount of enzyme in the two beans was compared. And the activity of the lipase on different substrates, such as lard, olive oil and ethyl butyrate, was estimated.

Experimental Work.

Analytical Methods.

In following Falk's method^{14,17} unsatisfactory results were obtained when such substrates as lard, olive oil, castor oil and soy oil were used. It was thought that the cause for this trouble was in the titration of organic acids in a watery medium, in which case the acids would not be in solution. Tests were made to determine this by the following method. Olive oil was saponified with potassium hydroxide and the resulting fatty acids purified. 0.1 cc. of these fatty acids was used in every case.

¹ Falk and Hamlin, *THIS JOURNAL*, 35, 210 (1913).

² Green, *Proc. Roy Soc.*, 48, 370 (1890).

³ Nicloux, *Mem. soc. c. Biol.*, 56, 701, 839, 868 (1904).

⁴ Hoyer, *Z. physiol. Chem.*, 50, 414 (1904).

⁵ Taylor, *J. Biol. Chem.*, 2, 87 (1906).

⁶ Astrid and Euler, *Z. physiol. Chem.*, 51, 244 (1907).

⁷ Kastle and Loevenhart, *Am. Chem. J.*, 24, 507 (1900).

⁸ Connstein, *Ergebnisse Physiol. Biochem.*, 3, 194 (1904).

⁹ Falk and Nelson, *THIS JOURNAL*, 34, 741 (1912).

¹⁰ Pekelbaring, *Z. physiol. Chem.*, 81, 355 (1912).

¹¹ Connstein, Hoyer, Wartenberg, *Ber.*, 35, 3988 (1902).

¹² Terroine, *Biochem. Z.*, 32, 429 (1910).

¹³ Falk, *THIS JOURNAL*, 36, 1, 1047 (1914).

¹⁴ Haubert, *Compt. rend. soc. biol.*, 124, 778 (1897).

¹⁵ Kastle and Loevenhart, *Am. Chem. J.*, 24, 491 (1900).

¹⁶ Falk, *THIS JOURNAL*, 37, 649 (1915).

¹⁷ Falk and Nelson, *ibid.*, 34, 735 (1912).

TABLE I
Titration of 0.1 cc of Fatty Acids in Various Media

25 cc of water	25 cc of water and 30 cc of alcohol	25 cc of water, 30 cc of alcohol, 10 cc of ether	35 cc of water, 30 cc of alcohol, 10 cc of ether	25 cc of absolute alcohol
1.70	2.40	3.00	3.00	2.90
1.80	2.30	3.00	2.95	2.85
1.60	2.40	3.00	2.90	3.05
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1.70	2.36	3.00	2.95	2.93

These results indicate that it is impossible to titrate all of the organic acid in a water medium.

To show that it is impossible to use the method employed by Falk, and Pennington and Hepburn,¹ two series of complete determinations were made. The first series, which is given in Table II, is the result of the titrations when made without the addition of alcohol and ether. The second series, Table III, is the result of the titrations after the addition of alcohol and ether. The differences given in the tables are the differences in titrations before and after incubation.

TABLE II

Substrate	% HCl Acidity medium	Acid and substrate difference Cc	Acid and enzyme difference Cc	Acid substrate and enzyme, difference Cc	Lipase action Cc
Lard	0.1	0.1	0.2	1.5	1.2
Olive oil	0.1	0.1	0.2	1.2	0.9
Lard	0.2	0.2	0.2	0.9	0.5
Olive oil	0.2	0.2	0.2	1.6	1.2

Av., 0.95

TABLE III

Substrate	% HCl Acidity medium	Acid and substrate difference Cc	Acid and enzyme difference Cc	Acid, substrate and enzyme difference Cc	Lipase action Cc
Lard	0.1	0.0	0.2	2.3	2.1
Olive oil	0.1	0.3	0.2	2.2	1.7
Lard	0.2	0.0	0.2	1.4	1.2
Olive oil	0.2	0.1	0.2	2.3	2.0

Av., 1.75

Considering these results, it is obvious that all of the acid is not measured when a direct titration is made. It was, therefore, decided to use the alcohol-ether method of titration.

There was the further possibility that error might arise by reason of undissolved fat, since fatty acids are more soluble in it than in any combination of water, alcohol and ether. A series of experiments was carried out to determine the amount of oil that would dissolve in a small

¹ Pennington and Hepburn, *THIS JOURNAL*, 34, 210 (1912).

quantity of water on the addition of a fixed amount of ether and alcohol. In 25 cc. of water, the amount used by some investigators,¹ it was found that 0.3 cc. of fat would dissolve on the addition of 50 cc. of alcohol and 20 cc. of ether.

It was found that the method of putting the materials together was important. The more intimate the contact of substrate and enzyme, the greater the activity of the lipase. Thorough breaking up and dissemination of the material through the liquid conduces to the best results. Even those titrated immediately show smaller values if not broken up.

In this work, then, the following method² was used: castor beans³ freed from husks by hand were coarsely ground, washed with ether, ground finely, extracted with ether for a week or more in a Soxhlet apparatus, and finally passed through a No. 40 sieve.⁴ Experiments with castor bean with and without the seed coat showed nearly twice the activity without the thick husk⁵ as compared with the whole bean preparation. In these experiments the enzyme preparations used were castor bean husk-free, and soy bean with the husk, otherwise similarly prepared.

The method of procedure in the determination of lipase activity was as follows: 0.2 g. of the lipase preparation was placed in a 150 cc. Erlenmeyer flask. Upon this 0.3 cc. of substrate was poured and the two shaken together so that all of the bean powder was saturated with the substrate. 20 or 25 cc. of solution was added and any lumps broken up. All experiments were made in triplicate. Three flasks containing substrate and acid, 3 flasks containing enzyme and acid, and 3 containing enzyme, substrate and acid, were placed in a thermostat⁶ and incubated⁷ at 38° for 24 hours. A similar series of 9 was prepared at the same time and titrated immediately. In all cases, before titrating, 20 cc. of ether and 50 cc. of 95% neutral alcohol were added⁸ and the flask vigorously shaken.⁹ The end-point, using 1.0% phenolphthalein in 95% alcohol, was a deep pink¹⁰ which lasted 30 seconds. Thymol was used as an anti-septic, 20 cc. of acid solution was used in all experiments except for 0.0 and 0.1 percentages, in which cases 25 cc. was used. To keep the volume of the standard alkali added less than 20 cc., 2 strengths were employed in some cases. 5.0 to 10.0 cc. of 0.5 *N* alkali was first added

¹ Falk and Nelson, *THIS JOURNAL*, 34, 741 (1912).

² Taylor, *J. Biol. Chem.*, 1, 87 (1906).

³ The castor beans were obtained from the Baker Castor Oil Co., New York.

⁴ Falk and Sugiura, *THIS JOURNAL*, 37, 218 (1915).

⁵ Nicloux, *Mém. soc. c. Biol.*, 56, 701, 839, 868 (1904).

⁶ Sigmund, *Sitzb. Akad. Wiss., Wien*, 407, 328 (1891).

⁷ Kastle and Loevenhart, *Am. Chem. J.*, 24, 491 (1900).

⁸ Allen, "Commercial Organic Analysis," II, part I, 3rd Ed., 104 (1899).

⁹ Lewkowitsch, "Chemistry, Technology and Analysis of Oil, Fats, and Waxes, Etc.," 3rd Ed., 277 (1904).

¹⁰ Falk and Nelson, *This Journal*, 34, 741 (1912).

and the titration completed with 0.1 *N* solution. All results are recorded in terms of 0.1 *N* standard.

The olive oil used was "Superfine" grade from Lautier Fils, Grasse. The butyric acid ester was Merck's "Concentrated Ethyl Butyrate." And the lard¹ was vacuum-kettle rendered, of fine texture and became liquid at 32°. The acid chosen was hydrochloric and the concentrations varied from 0.0 to 1.0% with intervals of 0.1%.

I. Castor Bean.

The determinations cover a series of tests of the lipolytic activity of the castor bean for the 3 substrates, lard, olive oil and ethyl butyrate, in an acid medium of various strengths. In the titrations made in triplicate the variations were very small, not exceeding 0.2 cc. The ethyl butyrate was the most subject to slight fluctuations.

The results obtained by the method outlined above are given in Tables IV to VII.

TABLE IV.
Action of Castor Bean Lipase on Lard.

Acidity medium % HCl	Acid and substrate, difference Cc	Acid and enzyme, difference Cc	Acid, substrate and enzyme, difference Cc
0.0	0.0	0.6	0.8
0.1	0.0	0.2	2.3
0.2	0.0	0.2	1.4
0.3	0.0	0.0	1.1
0.4	0.1	0.6	2.0
0.5	0.0	0.3	1.9
0.6	1.2	0.5	0.9
0.7	1.4	0.5	1.1
0.8	0.8	0.4	1.1
0.9	1.0	1.2	1.7
1.0	1.5	0.7	1.5

TABLE V.
Action of Castor Bean Lipase on Olive Oil.

Acidity, medium, % HCl	Acid and substrate, difference, Cc	Acid and enzyme, difference, Cc	Acid, substrate and enzyme difference, Cc
0.0	0.0	0.6	0.6
0.1	0.3	0.2	2.2
0.2	0.1	0.2	2.3
0.3	0.0	0.0	1.3
0.4	0.2	0.6	0.9
0.5	0.2	0.3	0.9
0.6	1.1	0.5	1.8
0.7	0.9	0.5	1.3
0.8	1.0	0.4	0.8
0.9	0.9	1.2	1.5
1.0	1.1	0.7	0.8

¹ The lard was furnished by Armour and Company, Chicago.

TABLE VI
Action of Castor Bean Lipase on Ethyl Butyrate.

Acidity, medium % HCl	Acid and substrate, difference Cc	Acid and enzyme, difference Cc	Acid, substrate and enzyme difference Cc
0.0	0.0	0.6	0.6
0.1	3.3	0.2	2.0
0.2	5.8	0.2	2.6
0.3	7.3	0.0	5.8
0.4	8.9	0.6	8.7
0.5	8.7	0.3	10.2
0.6	10.4	0.5	11.7
0.7	12.5	0.5	10.6
0.8	13.7	0.4	11.6
0.9	14.6	1.2	11.6
1.0	14.9	0.7	11.4

TABLE VII
Action of Castor Bean Lipase on Different Substrates

Acidity medium % HCl	Lard Cc	Olive oil Cc	Ethyl butyrate Cc
0.0	+0.2	+0.0	-0.0
0.1	+2.0	+1.6	-1.5
0.2	+1.2	+2.0	-3.4
0.3	+1.1	+1.1	-1.4
0.4	+1.3	+0.1	-0.8
0.5	+1.6	+0.4	+1.2
0.6	-0.8	+0.2	+0.8
0.7	-0.8	-0.1	-2.4
0.8	-0.1	-0.6	-2.5
0.9	-0.5	-0.6	-4.2
1.0	-0.5	-1.0	-4.2

Discussion.

The values in Tables IV, V and VI are obtained by subtracting the titrations before incubation from those after incubation, and are expressed in cc. of 0.1 *N* reagent. They represent the mean of triplicate determinations. In order to conserve space these separate determinations and others, also, have been omitted.

In Table IV, Acid and Substrate column, successive differences are 0.0 cc. with one exception, up to 0.6%; from 0.6% to 1.0% they vary from 0.8 cc. to 1.4 cc. The differences are larger in the acid and enzyme column up to 0.6%. Except for 0.9%, there is no increase in this column for stronger acid solutions. Due to the combination of enzyme and substrate, and the varying influence of different percentages of acidity on each, and on the combination, the third column shows a less uniform variation. Here they differ from 0.8 cc. to 2.3 cc.

Table V contains differences for the substrate olive oil. Comparing the differences in the acid and substrate column with those in the acid

and enzyme column, the variation is larger in the latter column up to 0.6%. From 0.6% to 1.0% the effect of the acid on the olive oil is greater than on the enzyme except in the case of 0.9% acid. As previously noted, the combination of acid, substrate and enzyme produces the greatest differences, the largest being 2.3 cc.; the smallest, 0.6 cc.

Table VI gives the differences in the determination of the action of castor bean lipase on ethyl butyrate. They show a steady increase from 0.0 cc. to 14.9 cc. This indicates hydrolysis of the substrate with weak acid solution which was not shown when lard and olive oil were used in corresponding strengths of acid. It is, therefore, doubtful whether it is advisable to substitute ethyl butyrate for the more complex esters of the fatty acids such as olive oil, palm oil, lard, etc., in experiments with fat-splitting enzymes.

The results in Table VII are obtained by subtracting the sum of the "difference" Col. 1 and 2 from Col. 3, as given in Tables IV, V and VI, and show the comparative lipase action on the 3 substrates, lard, olive oil and ethyl butyrate. From this table it is apparent, first, that castor bean lipase is active toward the substrates lard, olive oil and ethyl butyrate in an acid medium up to 0.7%; second, that the optimum acidity is approximately 0.6% for the 3 substrates; third, that castor bean lipase is active toward ethyl butyrate in 0.5 and 0.6% acidity only; and fourth, that this lipase is more active toward lard and olive oil than toward ethyl butyrate.

These results are more or less in agreement with those obtained by other workers. The experiments of Green¹ led him to the conclusion that the lipase action was hindered by the presence of even small amounts of acid. This may have been due to his method of lipase preparation. Armstrong and Gosney² found that "Ricinus lipase has its maximum activity when the acidity does not exceed that of the oleic acid." It may be that such equilibrium is reached at approximately 0.5% acidity. H. E. Armstrong³ found "Ricinus enzyme to have but little action on ethyl butyrate." Loevenhart⁴ found entirely different results when he substituted amyl salicylate for ethyl butyrate with liver-lipase extract. Connstein had better results with olive oil, castor oil and palm oil than with ethyl butyrate and other simple esters when acted upon by castor bean lipase.

II. Soy Bean.

The seed-coat of the soy bean is comparatively thin so that its presence does not materially alter the lipase activity. Two soy bean prepara-

¹ Green, *Proc. Roy. Soc.*, 48, 370 (1890).

² Armstrong and Gosney, *Proc. Roy. Soc. (B)*, 88, 176 (1914).

³ Armstrong, *Proc. Royal Soc. (B)*, 76, 606 (1903).

⁴ Loevenhart, *J. Biol. Chem.*, 51, 11, 393 (1906-7).

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beans were tried for relative activity with and without the husk. The following table shows the results with olive oil and 0.2% hydrochloric acid. S. B. I is with seed-coat and S. B. II without.

COMPARATIVE TESTS OF SOY BEAN WITH AND WITHOUT SEED-COAT.							
Acid and substrate difference.		Acid and enzyme difference.		Acid, substrate and enzyme difference.		Lipase action.	
S. B. I.	S. B. II.	S. B. I.	S. B. II.	S. B. I.	S. B. II.	S. B. I.	S. B. II.
0.1	0.1	0.1	0.2	0.5	0.7	0.3	0.4

In these experiments the soy bean preparation was made from the whole bean, otherwise prepared as was the castor-bean powder. The procedure was the same, *i. e.*, 0.2 g. portions were placed in 150 cc. Erlenmeyer flasks. Over this powder 0.3 cc. of substrate was poured, shaken together to insure through contact, and the mass broken up and completely scattered through the liquid. The ether-alcohol method of titration was used, all experiments being made in triplicate. The variation among these triplicates was small, being most marked in the case of ethyl butyrate.

Tables VIII to XI give the results in these determinations.

TABLE VIII.
Action of Soy Bean Lipase on Lard.

Acidity medium, % HCl.	Acid and substrate, difference, Cc.	Acid and enzyme, difference, Cc.	Acid, substrate and enzyme, difference, Cc.
0.0	0.0	0.4	0.8
0.1	0.0	0.4	0.5
0.2	0.0	0.1	0.6
0.3	0.0	0.4	0.9
0.4	0.1	0.5	1.2
0.5	0.0	0.4	0.8
0.6	1.2	1.9	2.1
0.7	1.4	1.8	2.5
0.8	0.8	1.0	1.7
0.9	1.0	1.5	2.3
1.0	1.3	1.5	2.4

TABLE IX.
Action of Soy Bean Lipase on Olive Oil.

Acidity medium, % HCl.	Acid and substrate, difference, Cc.	Acid and enzyme, difference, Cc.	Acid, substrate and enzyme, difference, Cc.
0.0	0.0	0.4	0.6
0.1	0.3	0.4	0.9
0.2	0.1	0.1	0.5
0.3	0.0	0.4	0.8
0.4	0.2	0.5	1.2
0.5	0.1	0.4	0.8
0.6	1.0	1.9	2.1
0.7	0.9	1.8	2.6
0.8	1.0	1.0	1.7
0.9	0.9	1.5	2.3
1.0	1.1	1.5	2.1

TABLE X.

Action of Soy Bean Lipase on Ethyl Butyrate.

Acidity medium. % HCl	Acid and sub- strate, difference Cc	Acid and en- zyme, difference Cc	Acid, substrate and enzyme, difference. Cc.
0.0	0.0	0.4	0.4
0.1	3.3	0.4	2.8
0.2	5.8	0.1	3.5
0.3	7.2	0.4	6.9
0.4	8.9	0.5	9.9
0.5	8.7	0.4	9.4
0.6	10.4	1.9	12.5
0.7	12.5	1.8	14.7
0.8	13.7	1.0	14.9
0.9	14.6	1.5	15.9
1.0	14.9	1.5	15.6

TABLE XI.

Action of Soy Bean Lipase on Different Substrates.

Acidity medium % HCl	Lard Cc	Olive oil. Cc	Ethyl butyrate. Cc.
0.0	+0.4	+0.2	-0.0
0.1	+0.1	+0.2	-0.9
0.2	+0.5	+0.3	-2.4
0.3	+0.5	+0.4	-0.7
0.4	+0.6	+0.5	+0.5
0.5	+0.4	+0.3	+0.3
0.6	-1.0	-0.8	+0.2
0.7	-0.7	-0.1	+0.4
0.8	-0.1	-0.3	+0.2
0.9	-0.2	-0.2	-0.2
1.0	-0.4	-0.5	-0.8

Discussion.

Tables VIII, IX and X are made up of the differences of titrations before and after incubation. Mean values based upon triplicate determinations were used to obtain the results.

Table VIII is for the differences of titration with soy bean lipase on lard. It will be noticed that there is no incubation effect up to 0.6% acidity. The hydrolysis of the fat is shown by the increase in differences from 0.6% to 1.0% acid solution, the largest being 1.4 cc. in the acid and substrate column. In the acid and enzyme column the greatest difference is 1.9 cc. But in the third column the maximum difference is 2.5 cc. and the minimum is 0.5 cc.

In Table IX, where the differences for soy bean lipase on olive oil are given, the greatest difference in Col. 1 is 1.1 cc. for 1.0% acid. In Col. 2 the greatest difference is 1.9 cc., while in Col. 3, or in acid, substrate and enzyme combination, the largest value is 2.6 cc. in a 0.7% hydrochloric acid medium.

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Table X gives the differences of soy bean lipase action on ethyl butyrate. It is noticeable that there is a very marked effect of the acid upon the substrate, the greatest value being 14.9 cc. for 1.0% acidity. The decrease in the effect is gradual from 1.0% to 0.0% acidity. In the third column, where the differences for the mixture of acid, substrate and enzyme are given, a gradual increase is observed from 0.4 cc. to 15.9 cc.

Table XI is a comparison of the lipase action of soy bean upon the 3 substrates, lard, olive oil and ethyl butyrate. The maximum acidity in which lipase action takes place is 0.8%. This is for ethyl butyrate. For lard and olive oil the maximum acidity is 0.5%. The maximum value is 0.6 cc. for lard, 0.5 cc. for olive oil, and 0.5 cc. for ethyl butyrate. The optimum acidity for the 3 substrates is 0.4%. The range of acidity in which there is positive action is 0.0 to 0.5%, inclusive, for lard and olive oil, and 0.4 to 0.8% for ethyl butyrate. It is interesting to note that the range of acidity of the medium in which ethyl butyrate is split is shorter than the range for lard and olive oil. Also that the range includes only a small part of the extreme ends of the ranges for lard and olive oil.

TABLE XII
Lipase Action of Soy and Castor Beans on Lard

Acidity medium % HCl	Soy bean Cc	Castor bean Cc
0.0	+0.4	+0.2
0.1	+0.1	+2.0
0.2	+0.5	+1.2
0.3	+0.5	+1.1
0.4	+0.6	+1.3
0.5	+0.4	+1.6
0.6	—0	—0.8
0.7	—0.7	0.8
0.8	—0.1	0.1
0.9	—0.2	0.5
1.0	—0.4	—0.5

TABLE XIII
Lipase Action of Soy and Castor Beans on Olive Oil

Acidity medium % HCl	Soy bean Cc	Castor bean Cc
0.0	+0.2	+0.0
0.1	+0.2	+1.7
0.2	+0.3	+2.0
0.3	+0.4	+1.3
0.4	+0.5	+0.1
0.5	+0.3	+0.4
0.6	—0.8	+0.2
0.7	—0.1	—0.1
0.8	—0.3	—0.6
0.9	—0.2	—0.6
1.0	—0.5	—1.0

TABLE XIV.

Lipase Action of Soy and Castor Beans on Ethyl Butyrate.		
Acidity medium. % HCl	Soy bean Cc	Castor bean. Cc
0.0	-0.0	-0.0
0.1	-0.9	-1.5
0.2	-2.4	-3.4
0.3	-0.7	-1.4
0.4	+0.5	-0.8
0.5	+0.3	+1.2
0.6	+0.2	+0.8
0.7	+0.4	-2.4
0.8	+0.1	-2.5
0.9	-0.2	-4.2
1.0	-0.8	-4.2

Tables XII, XIII and XIV show the comparative lipase activity of castor and soy beans on the substrates, lard, olive oil and ethyl butyrate. In Table XII where the action of the enzyme is shown on lard, the range gives a positive action for 0.0 to 0.5%, inclusive, and negative for the remainder. The amount of lipase action of soy bean varies from 0.1 to 0.6 cc. The range of the acidity of the medium in which fat splitting takes place is from 0.1 to 0.5%. The amount of lipase action of castor bean ranges from 0.2 to 2.1 cc. The acidity of the medium in which action takes place amounts to 0.0 to 0.5%. The largest negative value for each enzyme is at 0.6%. For soy bean this value is 1.0 cc. and for castor bean 0.8 cc. Tests with acidities up to 2.0% gave still larger negative results.

Comparing the enzyme action of soy bean with that of castor bean on lard, some differences are evident. First, the maximum activity of castor bean is 2.0 cc., that of soy is 0.6 cc. Second, the maximum activity for castor bean occurs at 0.1% acidity, while for soy bean it is at 0.4%. And, third, for both enzymes the maximum acidity for lipase activity is 0.5%.

These results are, in general, comparable to those of other investigators. Connstein, Hoyer and Wartenberg¹ found that hydrolysis was not hindered by as much as 2.0% of acetic acid, and that 0.1 *N* sulfuric acid hastened fat-splitting. This is approximately 0.5% concentration. Further comparison with their results is impossible because of difference in material and method. Armstrong² obtained 4.1 g. of oleic acid from 5.0 cc. of olive oil with one g. of fat-free castor bean in 0.03 *N* (approximately 0.15%) sulfuric acid, after 18 hours of incubation at 38°.

In Table XIII is a comparison of the lipase action of both beans on olive

¹ Connstein, Hoyer and Wartenberg, *Ber.*, 35, 3988 (1902).

² Armstrong, *Proc. Roy. Soc. (B)*, 76, 606 (1903).

oil. The positive action range for this substrate is from 0.0 to 0.5%, inclusive, for soy bean and from 0.0 to 0.6% for castor bean. For the remainder of the percentages of acidity the values are negative. The greatest soy bean activity, 0.5 cc., is manifest at 0.4%. For castor bean the maximum activity is 2.0 cc. at 0.2%. The maximum negative value is 0.8 cc. for soy bean at 0.6% and 1.0 cc. for castor bean at 1.0%. Higher percentages of acidity gave increased negative results. Therefore, using olive oil as a substrate, the comparative action of lipases from soy and castor beans is as follows: first, the castor bean is very much more active; and second, the range of acidity of the medium is practically the same in both cases. These results are very similar to those obtained with lard.

Table XIV gives the results of the action of soy and castor bean lipases upon ethyl butyrate. Soy bean shows a negative activity up to 0.4% acid, positive to 0.9%, and negative again for 0.9 and 1.0%. For castor bean lipase all values are negative except 0.5 and 0.6%. The highest positive value for soy bean lipase is 0.5 cc. at 0.4%. For castor bean, 1.2 cc. at 0.5% is the greatest positive value. Stronger acidity gave larger negative results. A comparison of the action of the enzymes of the 2 beans on ethyl butyrate shows, first, that soy bean lipase is active over a greater range of acidity, but activity is less than that of castor bean lipase for a given strength of acid; second, that the maximum activity for castor bean lipase is 1.2 cc. at 0.5%; for soy bean it is 0.5 cc. at 0.4% acidity; and third, that the activity of soy bean lipase ceases at 0.9% and that of castor bean lipase at 0.7%.

Comparing the various tables, especially Tables VII and XI, the following features are apparent: first, that castor and soy bean lipases are active toward the substrates, lard, olive oil and ethyl butyrate, in 0.4 and 0.5% medium; second, that the optimum acidity for castor and soy bean lipase is approximately 0.5% for lard and olive oil; third, that neither soy nor castor bean lipase is active toward ethyl butyrate in less than 0.4% acidity; fourth, that soy bean lipase does not show as great activity values as does castor bean lipase—the maximum ratio being 2.0 cc. to 0.6 cc.; fifth, with ethyl butyrate the castor bean lipase is active over a smaller range of acidity than is soy bean lipase; and sixth, that both soy and castor bean lipases are more active toward olive oil and lard than toward ethyl butyrate.

A graphic representation of the data would show that the castor bean has the more intense activity, that the forms of the curves for acidity of media and amount of activity do not have characteristic differences, and that the ranges of activity in increasing strengths of acid do not characteristically differ. These facts would go far in leading one to the conclusion that castor and soy beans contain the same lipase or lipases

but in different quantity. With this Falk and Sugiura,¹ in the main, agree; and Falk² concluded from his work with lipases from castor bean, soy bean, etc., that marked similarities in action are shown by lipases from different sources. He did not compare the relative amounts of activity for any range of acidity. Armstrong³ found castor bean to have little action on ethyl butyrate. Taylor⁴ recommended the use of triacetin as a substrate. Connstein⁵ found that ethyl butyrate was acted upon to a much less satisfactory extent than was olive oil, castor oil and palm oil.

Summary and Conclusion.

The lipases of the castor and soy bean were studied with relation first to their ranges and amounts of activity in a watery medium with acid reaction and second to their actions in these media on 3 substrates, lard, olive oil and ethyl butyrate. The methods used in making these determinations were investigated.

The following conclusions were reached:

First, when lard or olive oil is used as a substrate, the liberated fatty acids cannot be titrated in a water mixture, with an aqueous standard alkali solution. Ether and alcohol must be added before titration in at least sufficient quantity to make a single and complete solution of all of the fat.

Second, of the preparations used, the castor bean lipase was more intense in its action than the soy bean lipase.

Third, the ranges of acidity of the media in which action took place were practically the same for castor and soy bean lipase, and were independent of the kind of substrate.

Fourth, lard and olive oil afforded practically equal degrees of activity in the various acidities and ranges of acidity in which activity took place.

Fifth, ethyl butyrate as a substrate differed characteristically from lard and olive oil in that the degree of activity was smaller and the range of acidity in which action took place was much higher and shorter.

The above conclusions in connection with the data presented, lend proof to the following hypotheses:

First, the castor bean lipase splits esters of the fatty acids to a greater extent than does soy bean lipase.

Second, soy and castor beans contain the same lipase or lipases.

Third, both soy and castor beans contain more than one lipase.

This work was outlined and begun under the direction of the late Dr.

¹ Falk and Sugiura, *THIS JOURNAL*, 37, 218 (1915).

² Falk, *ibid.*, 37, 649 (1915).

³ Armstrong, *Proc. Roy. Soc. (B)*, 76, 606 (1905).

⁴ Taylor, *J. Biol. Chem.*, 2, 87 (1906).

⁵ Connstein, *Ergebnisse Physiol. Biochem.*, 3, 194 (1904).

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[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

ON THE ORIGIN OF THE HUMIN FORMED BY THE ACID HYDROLYSIS OF PROTEINS. IV. HYDROLYSIS IN THE PRESENCE OF ALDEHYDES. III. COMPARATIVE HYDROLYSIS OF FIBRIN AND GELATIN IN THE PRESENCE OF VARIOUS ALDEHYDES.¹

By GEORGE E. HOLM AND ROSS AIKEN GORTNER

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In the earlier papers of this series, by Gortner and Blish,² Gortner,³ and Gortner and Holm,⁴ we have studied the effect of certain aldehydes upon the acid hydrolysis of proteins with especial reference to the origin and mode of formation of the "humin" fraction. Detailed observations were made using various carbohydrates, which under the conditions of the experiment would yield furfural and formaldehyde, with a few observations, where benzaldehyde was present. It was noted that the hydrolysis of a protein in the presence of an aldehyde markedly altered the nitrogen distribution, so much so that when formaldehyde was present in excess the resulting nitrogen distribution bore no resemblance to the values obtained in the absence of the aldehyde. The most noteworthy changes in the nitrogen distribution were in the ammonia and humin fractions, but the fact that an excess of formaldehyde over that required to cause maximum humin formation apparently unites with the α -amino groups so that they no longer react with nitrous acid, causes the remaining nitrogen fractions to lose all resemblance to those of a normal hydrolysate.

We have furthermore shown that in all probability the black insoluble humin nitrogen is derived from the interaction of tryptophane and an aldehyde. However, tyrosine also reacts with aldehydes to form com-

¹ Presented before the Biological Division at the Philadelphia meeting of the American Chemical Society, Sept. 2-6, 1919. Published with the approval of the Director as Paper No. 190, Journal Series of the Minnesota Agricultural Experiment Station.

² R. A. Gortner and M. J. Blish, "On the Origin of the Humin Formed by the Acid Hydrolysis of Proteins," *THIS JOURNAL*, **37**, 1630-36 (1915).

³ R. A. Gortner, "The Origin of the Humin Formed by the Acid Hydrolysis of Proteins. II. Hydrolysis in the Presence of Carbohydrates and of Aldehydes," *J. Biol. Chem.*, **26**, 177-204 (1916).

⁴ R. A. Gortner and G. E. Holm, "On the Origin of the Humin Formed by the Acid Hydrolysis of Proteins. III. Hydrolysis in the Presence of Aldehydes. II. Hydrolysis in the Presence of Formaldehyde," *THIS JOURNAL*, **29**, 2477-2501 (1917).

pounds whose solubility depends upon the particular aldehyde present. Thus with formaldehyde the tyrosine-aldehyde compound is soluble in dil. hydrochloric acid and is thus readily separable from the tryptophane-aldehyde humin. On the other hand, certain experiments which we have reported seem to indicate that the tyrosine benzaldehyde compound is insoluble in the various concentrations of hydrochloric acid and is therefore not separable from the tryptophane-benzaldehyde humin. It, therefore, seemed advisable to extend our observations so as to include a more extended study of the effect of other aldehydes, especially benzaldehyde, upon the nitrogen distribution of proteins when the aldehyde has been present during the process of acid hydrolysis.

Experimental.

No fibrin such as that used in our previous experiments could be obtained. A sample of commercial "fibrin from blood" was, therefore, purified as follows. The fibrin was finely ground and brought into solution with a 0.2% solution of sodium hydroxide. The solution was filtered through 4 double cheese cloths and precipitated with hydrochloric acid. This precipitate was washed to the absence of chlorides by decantation, dried at a low temperature and ground. This product, free from blood and other impurities, was used in subsequent hydrolyses. The gelatin used was of the same sample as that used in our earlier studies.

In order to obtain comparative data regarding the action of different aldehydes upon the same protein preparations, it was, therefore, necessary to repeat certain of the experiments with formaldehyde using this new

TABLES I AND II—THE EFFECTS OF INCREASING AMOUNTS OF FORMALDEHYDE UPON THE ACID HYDROLYSIS OF GELATINE AND FIBRIN, RESPECTIVELY

TABLE I				
Amount (CH ₂ O) ₁ used G	Acid-insoluble humin nitrogen Mg	Ammonia nitrogen Mg	Acid-soluble humin nitrogen Mg	Total amino nitrogen Mg
0.00	0.12	4.58	0.35	319.67
0.05	0.14	5.00	0.57	314.04
0.10	0.13	6.30	0.50	307.00
0.25	0.13	9.43	0.48	295.97
0.50	0.10	19.27	0.50	174.99
1.00	0.05	30.40	0.47	229.15
2.50	0.07	44.75	0.28	120.10
3.00	0.03	51.45	0.35	34.77
TABLE II				
0.00	6.45	34.65	5.87	341.32
0.05	10.70	30.35	10.95	"
0.10	14.25	29.50	16.35	313.56
0.25	2.65	26.47	29.60	292.54
0.50	1.10	30.50	27.90	261.49
1.00	1.40	38.70	25.95	236.50
2.50	0.95	51.32	19.90	117.12
4.00	0.22	"	"	"

material. Besides formaldehyde the following aldehydes were used: benzaldehyde, acetaldehyde, butyric and isobutyric aldehyde.

The method of procedure was the same as that used in the former experiments with two exceptions: (1) Hydrolysis was continued for 24 hours only; (2) besides insoluble humin nitrogen, ammonia nitrogen and soluble humin nitrogen, the total amino nitrogen was determined upon the filtrate from the soluble humin. This method of procedure gave an indication of the effect of various aldehydes upon humin formation and also showed their effect upon the α -amino nitrogen of the various amino acids not involved in humin formation.

Tables I to IX show the effects of the various aldehydes upon the acid

TABLES III AND IV.—THE EFFECTS OF INCREASING AMOUNTS OF BENZALDEHYDE UPON THE ACID HYDROLYSIS OF GELATINE AND FIBRIN, RESPECTIVELY.

TABLE III.

Aldehyde used. Cc.	Acid-insoluble humin nitrogen Mg.	Ammonia nitrogen Mg.	Acid-soluble humin nitrogen. Mg.	Total amino nitrogen Mg.
0.00	0.12	4.58	0.35	319.67
0.05	0.49	4.60	0.30	318.90
0.10	0.55	4.70	0.34	319.30
0.25	0.67	4.65	0.30	317.10
0.50	0.67	4.33	0.35	322.61
1.00	0.82	5.00	0.27	318.53
2.50	0.86	7.55	0.38	323.20

TABLE IV.

0.00	6.45	34.65	5.87	341.32
0.05	10.50	33.00	2.60	340.10
0.10	13.50	32.50	1.90	340.10
0.25	15.17	33.00	3.40	336.77
0.50	16.25	33.50	3.60	324.16
1.00	18.35	33.30	3.60	320.54
2.50	24.55	33.54	2.72	313.95
5.00	24.30	34.31	4.15	{ 309.40 308.60

TABLE V.—THE EFFECT OF INCREASING AMOUNTS OF ACETALDEHYDE UPON THE ACID HYDROLYSIS OF GELATINE.

Aldehyde used Cc.	Acid-insoluble humin nitrogen. Mg.	Ammonia nitrogen. Mg.	Acid-soluble humin nitrogen Mg.	Total amino nitrogen Mg.
0.00	0.12	4.58	0.35	319.67
0.05	0.47	4.60	1.78	Not determined
0.10	0.90	4.77	3.16
0.25	1.60	5.10	4.26
0.50	4.80	4.57	6.00
1.00	12.10	4.32	6.56
2.50	22.93	4.00	7.88
5.00	41.75	6.00	6.10

hydrolysis of fibrin and gelatin, 3 g. of protein being used in each experiment. The data for acid insoluble humin have been plotted in the form of curves and are shown in Fig. 1.

TABLES VI AND VII.—THE EFFECTS OF INCREASING AMOUNTS OF BUTYRIC ALDEHYDE UPON THE ACID HYDROLYSIS OF GELATINE AND FIBRIN, RESPECTIVELY.

TABLE VI

Aldehyde used. Cc.	Acid-insoluble humin nitrogen. Mg.	Ammonia nitrogen. Mg.	Acid-soluble humin nitrogen. Mg.	Total amino nitrogen. Mg.
0.00	0.12	4.58	0.35	319.67
0.05	0.35	4.36		321.32
0.10	0.50	4.30	0.86	324.69
0.25	0.75	4.64	0.85	320.85
0.50	1.00	5.05	1.10	316.30
1.00	2.80	4.75	1.23	318.71
2.50	5.60	5.00	1.47	311.14
4.00	7.37	5.57	1.67	311.14

TABLE VII.

0.00	6.45	34.65	5.87	341.32
0.05	7.20	32.32	4.30	..
0.10	9.30	31.76	2.40	..
0.25	12.55	30.88	2.10	335.09
0.50	14.10	30.65	2.60	..
1.00	15.50	31.75	3.20	330.69
2.50	18.03	31.79	2.65	309.65
5.00	24.00	31.80	3.00	..

TABLES VIII AND IX —EFFECTS OF INCREASING AMOUNTS OF ISOBUTYRIC ALDEHYDE UPON THE ACID HYDROLYSIS OF GELATINE AND FIBRIN, RESPECTIVELY.

TABLE VIII.

Aldehyde used Cc.	Acid-insoluble humin nitrogen Mg.	Ammonia nitrogen. Mg.	Acid soluble humin nitrogen Mg.	Total amino nitrogen. Mg.
0.00	0.12	4.58	0.35	319.67
0.05	0.27	4.40	1.11	320.50
0.10	0.33	4.15	1.40	320.60
0.25	0.55	4.53	1.40	319.77
0.50	0.74	4.06	1.47	320.77
1.00	0.89	4.65	1.70	314.00
2.50	2.57	5.32	2.08	312.22
5.00	3.23	6.05	1.80	{ 307.7 307.14

TABLE IX.

0.00	6.45	34.65	5.87	341.32
0.05	7.37	31.70	6.35	338.45
0.10	9.42	31.66	5.12	337.18
0.25	11.23	30.00	4.25	328.41
0.50	13.57	30.00	4.33	332.10
1.00	12.97	30.93	4.55	328.50
2.50	20.80	31.00	4.15	..
5.00	23.10	30.85	4.00	..

Discussion.

The general reaction of formaldehyde upon these proteins has already been discussed in the paper by Gortner and Holm.¹

Benzaldehyde gives an entirely different reaction. If benzaldehyde is added to gelatin or fibrin in a 20% hydrochloric acid solution and allowed to stand, a dark blue color develops in the case of the fibrin but only a faint blue color in the gelatin solution. This is undoubtedly the blue color produced by benzaldehyde and tryptophane in an acid solution, and serves as an indication of the presence of this amino acid. We believe that this reaction may be developed so as to serve for the quanti-

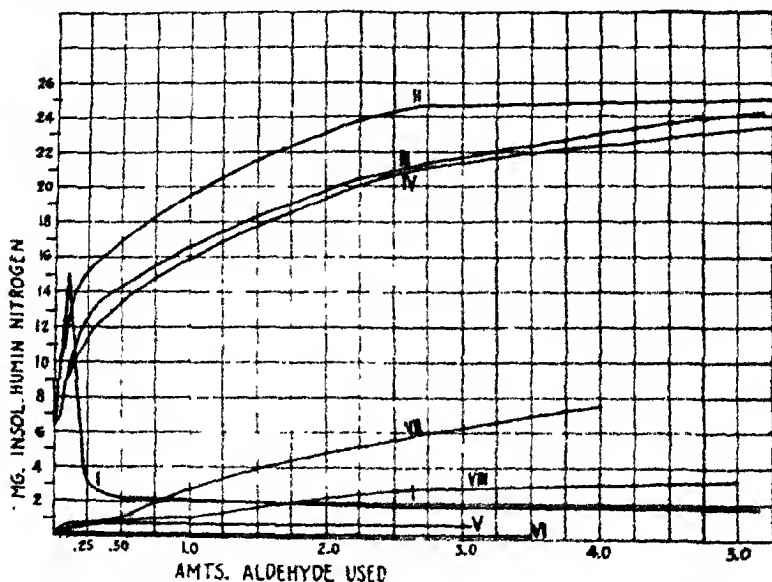


Fig. 1

Graph showing the insoluble humin nitrogen curves for Tables I to IX inclusive.

- | | |
|--------------------------------------|---|
| I.—Fibrin-formaldehyde curve. | V.—Gelatine-benzaldehyde curve. |
| II.—Fibrin-benzaldehyde curve. | VI.—Gelatine-formaldehyde curve. |
| III.—Fibrin-butyric aldehyde curve | VII.—Gelatine-butyric aldehyde curve. |
| IV.—Fibrin-isobutyric aldehyde curve | VIII.—Gelatine-isobutyric aldehyde curve. |

tative estimation of tryptophane colorimetrically, but the final experiments on this work have had to be delayed until the humin work reached a point where it could be suspended for a time. If a solution of fibrin and benzaldehyde in 20% hydrochloric acid is hydrolyzed, a black humin is formed. With increased amounts of benzaldehyde there is an increase in the amount of insoluble humin but no increase in ammonia or soluble

¹ *Loc. cit.*

humin. The insoluble humin rises to a constant value (see Curve II, Fig. 1) at which point a dark plastic mass floats in the benzaldehyde layer upon a remaining light straw-colored hydrolysate. Gortner¹ has shown that when fibrin is hydrolyzed with hydrochloric acid in the presence of benzaldehyde a large percentage of the nitrogen of both tryptophane and tyrosine remains in the "acid-insoluble" humin. The insoluble humin at the maximum point in this case therefore is undoubtedly derived from the tryptophane and tyrosine present in the gelatin and fibrin.

Gortner and Holm¹ have already shown that the insoluble humin obtained in the presence of formaldehyde is derived almost exclusively from tryptophane so that by utilizing both the formaldehyde and benzaldehyde data one may estimate at least the minimal tryptophane and tyrosine content of a protein. Thus in the case of fibrin our data indicate a content of 3.47% of tryptophane and at least 6.13% of tyrosine,² while in the case of gelatine³ the values are 0.035% and 0.47%, respectively.

In the case of formaldehyde the decrease in α -amino nitrogen is probably due to formation of methylene linkages. Probably no such reaction occurs with benzaldehyde as may be seen in the case of gelatin hydrolyzed with an excess of benzaldehyde. *The total amino nitrogen value remains practically constant.* In the case of fibrin, however, the decrease in amino nitrogen is slightly more than can be accounted for by the removal of amino nitrogen through the formation of insoluble humin, when we attribute the formation of the humin to tryptophane and tyrosine. The data at present are insufficient to explain the slight additional decrease of amino nitrogen above that which is removed through the formation of humin.

The effects of acetaldehyde, butyric aldehyde and isobutyric aldehyde are somewhat similar. Acetaldehyde polymerized (?) readily in acid solution forming large masses of black amorphous material. In the case of gelatin it was possible to gain some idea of the amount of nitrogen in this black amorphous substance, while in the case of fibrin even small quantities of acetaldehyde produced such a large bulk of this amorphous material that no systematic study could be made. The difference in the amounts of "insoluble humin" formed by acetaldehyde with gelatin and

¹ *Loc. cit.*

² The figures for tryptophane are, we believe, a very accurate measure of the quantity of this amino acid which is present in the protein. The figures for tyrosine, on the other hand, are, in all probability, minimal values, for there appears to be a solubility factor, and possibly also an adsorption factor involved. We have not yet studied these phenomena in detail.

³ Gelatin is supposed to contain neither tyrosine nor tryptophane. Possibly these amino acids are absent from extremely pure gelatin, but we have as yet found no sample from which we believe either amino acid to be entirely absent.

fibrin indicated, however, that the reaction is not a simple polymerization with simultaneous adsorption or occlusion of amino acids, but that other reactions are involved. As yet no means of identifying the nature and extent of these reactions has been devised. Butyric and isobutyric aldehydes, like acetaldehyde, formed black, insoluble residues when boiled in a 20% hydrochloric acid solution, but do so much less readily than does acetaldehyde. Their effect upon the hydrolysis of gelatin and fibrin is apparently somewhat analogous to that of benzaldehyde. They affect chiefly the acid-insoluble humin, increasing it to an approximately constant value, forming a dark layer floating upon a straw-colored solution. The effect in the case of gelatin shows the part that polymerization plays in increasing the insoluble humin nitrogen. With benzaldehyde this fraction remains constant but with butyric and isobutyric aldehydes it increases very slowly with increased amounts of aldehyde, but the increase is far from the amounts and proportionalities it should maintain if it were purely a chemical reaction. In short, the behavior of acetic, butyric and isobutyric aldehydes resembles more or less closely that of furfural, which Gortner¹ has already studied, reaching the conclusion that, inasmuch as both physical and chemical reactions are involved, no exact interpretation of the humin nitrogen figures can be made.

Difficulty was experienced in the determination of the α -amino nitrogen in hydrolysates where acetic, butyric and isobutyric aldehydes had been used. There was always a tendency to a formation of large amounts of gas when aliquots were treated with nitrous acid in the Van Slyke² apparatus. This may be accounted for by a small amount of aldehyde which may remain in loose combination with the amino acids and when treated with nitrous acid forms some non-absorbable gas. That all the gas evolved upon treatment with nitrous acid is not nitrogen and oxides of nitrogen is shown by the fact that the gas from samples of hydrolysates in which acetaldehyde, butyric or isobutyric aldehydes had been used would not come to constant volume over water for several hours, after the evolved gases had been shaken with the fresh alkaline permanganate.

These results, in so far as humin formation is concerned, only serve to confirm our conclusions which were drawn from the earlier data, *i. e.*, that "the formation of black acid-insoluble humin in a protein hydrolysate is due to a combination of tryptophane with some as yet unidentified aldehyde or ketone, and that the only part which any of the other known amino acids have in humin formation is to (perhaps) furnish some of their nitrogen to the humin fraction through either adsorption or occlusion." It may appear to some that the accuracy of this statement depends largely

¹ *Loc. cit.*

² D. D. Van Slyke, "The Quantitative Determination of Aliphatic Amino Groups. II," *J. Biol. Chem.*, 32, 275-284 (1917).

on the nature of the hypothetical aldehyde or ketone which we postulate must be present (or formed) in a protein hydrolysate before humin formation can take place. Thus from the above data it would appear probable that if the hypothetical aldehyde or ketone present in a protein preparation were similar to formaldehyde the acid-insoluble humin will be derived solely from tryptophane, excluding a small but negligible amount of other amino acids, not chemically concerned in humin formation which may be adsorbed on the tryptophane humin. If, however, the hypothetical compound were an aromatic aldehyde or one of the aliphatic aldehydes (other than formaldehyde) it would appear that both tryptophane and to a certain extent tyrosine should be involved in acid-insoluble humin formation.¹ All that we know of the nature of this hypothetical aldehyde is derived from experiments which have already been reported where tryptophane was added to zein, by Gortner and Blish² and to gelatin, by Gortner and Holm,³ respectively. In the zein experiment figure 1 g. of zein hydrolyzed alone yielded 0.7 mg. of humin nitrogen; hydrolyzed in the presence of 0.125 g. tryptophane, it yielded 7.7 mg. of humin nitrogen, and when 0.25 g. tryptophane was added 7.0 mg. of humin nitrogen was obtained, showing that the unknown component of the protein had been exhausted by the addition of 0.125 g. tryptophane so that none remained to react with a larger amount of tryptophane. Osborne and Liddle⁴ have found 3.55% of tyrosine in zein, so that it is obvious, in the light of our present knowledge, that tyrosine plus the hypothetical aldehyde of zein cannot produce any appreciable quantity of black, insoluble humin, but that tryptophane plus the unknown factor does produce such humin.

In the gelatin experiment 3 g. of gelatin hydrolyzed alone gave 0.25 mg. of insoluble humin nitrogen. When 0.10 g. of tyrosine was added 0.20 mg. of insoluble humin nitrogen was found, but when 0.075 g. of tryptophane was added the insoluble humin nitrogen amounted to 2.05 mg. Thus in both zein and gelatin the unknown factor in humin formation reacts only with tryptophane and not with tyrosine in forming humin nitrogen. In other words, it acts very similar to the formaldehyde of our experiments. For this reason we believe that, of the amino acids, tryptophane only furnishes any appreciable part in the formation of the black acid-insoluble humin.

¹ Formaldehyde does not differ radically from the other aldehydes for here the greater part of the humin formed by tyrosine is estimated in the "acid-soluble humin" fraction, that is, it is soluble in acid but relatively insoluble in the presence of calcium hydroxide.

² *Loc. cit.*

³ T. B. Osborne and L. M. Liddle, "Notes on the Analysis of Edestin and Zein" *Am. J. Physiol.*, 26, 295-304 (1910).

Summary.

In the experiments reported in the preceding pages fibrin and gelatin were hydrolyzed in the presence of formaldehyde, benzaldehyde, acetaldehyde, butyric aldehyde and isobutyric aldehyde with especial reference to the formation of the black, insoluble humin of protein hydrolysis and with incidental reference to the formation and composition of the "soluble humin" and the "ammonia" fractions. The following conclusions are evident:

1. The data in those experiments where formaldehyde was used confirm the earlier conclusions of Gortner and Holm.¹

2. When proteins are hydrolyzed in the presence of increasing amounts of benzaldehyde the acid-insoluble humin nitrogen rises rapidly to a maximum and the reaction appears wholly chemical. This increase is undoubtedly due to the presence of both tryptophane and tyrosine, since fibrin and gelatin both give an increase in insoluble humin nitrogen over the maximum insoluble humin nitrogen formed in the presence of formaldehyde approximately equal to the sum of the increase of the insoluble and soluble humin in the latter case.

3. The "ammonia" and "soluble humin" are not significantly altered when proteins are hydrolyzed in the presence of benzaldehyde.

4. The action of butyric and isobutyric aldehydes upon protein hydrolysis is analogous to the action of benzaldehyde with the exception that the former polymerize (?) readily permitting perhaps of some adsorption or occlusion of other nitrogen compounds

5. Acetaldehyde polymerizes (?) too readily in acid solution to give consistent and reliable results.

6. The total amino nitrogen in the filtrate from the soluble humin rapidly falls with the addition of increasing amounts of formaldehyde. This decrease is probably due to the formation of methylene linkages. On the other hand, hydrolysis in the presence of benzaldehyde, butyric and isobutyric aldehydes causes at the most only a slight decrease in the amino nitrogen figures over that which is removed by the soluble and insoluble humin.

7. Our data confirm the conclusion that the formation of the black acid-insoluble humin in a normal protein hydrolysate (only protein and acid present) is dependent upon the presence of tryptophane in the protein molecule, and the only part which any of the other known amino acids has in such humin formation is to (perhaps) furnish an insignificant amount of nitrogen to the humin fraction through either adsorption or occlusion.

ST. PAUL, MINN.

¹ Loc. cit.

CARBON MONOXIDE A RESPIRATION PRODUCT.

BY SETH C. LANGDON AND WALTER R. GALEY.

Received December 29, 1919.

In a paper presented by one of us¹ it was shown that there is present an average of 4% (by volume) of free carbon monoxide in the pneumatocyst (*i. e.*, the floater) of the giant Pacific Coast kelp *Nereocystis leutkeana*.

This unique occurrence of free carbon monoxide within a living plant at once raised the question as to its origin. The intimate chemical relation of carbon monoxide to formaldehyde and formic acid had long ago suggested its possible relation to photosynthetic processes. On the basis of the physiology and structure of the plant there were grounds for the consideration that the carbon monoxide might be a product of respiration.

The possibility of its formation due to the action of enzymes or to processes of decay was the first point investigated. Finely ground kelp was allowed to undergo autolysis in contact with sea water and the gases evolved were examined. No carbon monoxide was formed, but the gas consisted almost entirely of carbon dioxide and hydrogen.

The next step was to determine how rapidly carbon monoxide was formed within the living plant. The method of work and the subsequent discussion will be made more clear if preceded by a brief description of the plant.

Fig. 1 shows the plant as it rests almost submerged in the sea water, but anchored to the rock bottom and supporting the streaming fronds from the top of the hollow gas-filled stipe. The plants vary greatly in size; individuals are often 80 to 100 feet in length and

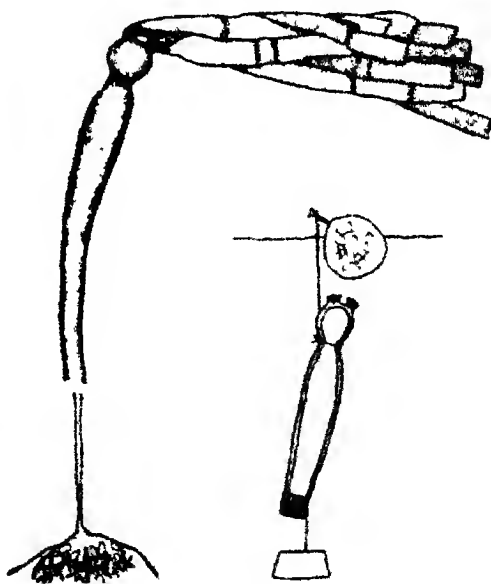


Fig. 1.

Fig. 2.

contain several liters of gas, usually at reduced pressures.² The inside of the gas cavity is relatively quite dry and is lined with a delicate web-like

¹ Langdon, *This Journal*, 39, 149 (1917).

² Frye, *Puget Sound Marine Sta. Pub.*, 1, 85 (1916)

structure, known as sieve tubes. The plant will withstand a great deal of mutilation and still continue to live and grow if kept in sea water.¹

It was found practicable to cut off the lower part of the stipe and in the upper part substitute a gas of known composition for that normally present in the pneumatocyst. The cut end was closed by a cork and the weighted plant submerged in the sea tied to a support as shown in Fig. 2. After a suitable interval and changes in the composition of the gas were determined by analysis.

In the first experiments, made primarily to determine the rate of formation of carbon monoxide, air was substituted for the kelp gas. This was accomplished by filling the cut stipe with sea water and then emptying. This process, repeated 3 or 4 times, removed the small bubbles of the original kelp gas that tended to adhere to the delicate sieve tube lining of the interior. The cut end of the now air-filled stipe was corked and the prepared plant anchored near the surface of the sea as previously described.

Analyses of the gases from a series of these cut and air-filled plants were made after various intervals of time. The typical data given in Table I show clearly the gradual formation of carbon monoxide. This is accompanied by a decrease in oxygen content and the appearance of carbon dioxide. The latter is undoubtedly due to processes of decay, since carbon dioxide is not present within the normal plant. In general, the cut and corked section of stipe remained sound enough to be tight for a week or ten days, although evidence of local decomposition was apparent.

The production of carbon monoxide when the stipe was filled with air was confirmed by a large number of determinations with different specimens. In most cases it appeared in quantities greater than 1%. Carbon monoxide was formed by sections cut from any part of the hollow stipe if these were filled with air, corked and similarly suspended in the sea. The leaves, more properly called fronds, seemed to bear no relation to the formation of the carbon monoxide for it was produced just as readily in specimens from which the fronds had been removed.

TABLE I.
Analyses of Gases in Air-Filled Stipes.

Time, start. Hrs.	CO ₂ . %.	CO. %.	O ₂ . %.
	0.0	0.0	20.8
24	0.3	0.0	16.5
48	0.0	0.4	13.0
73	0.6	1.0	7.0
97	1.0	3.2	6.2
110	1.1	4.5	5.0

¹ Fallis, *Puget Sound Marine Sta. Pub.*, 1, 1 (1916).

In all of the experiments detailed above, the test specimens, while anchored in the bay, were exposed to the light during the long summer day. The next step was to determine if the carbon monoxide would be formed in the dark.

For this purpose boxes were constructed which were light-tight but which would allow a ready flow of water through them. These boxes were one foot square and 18 feet long. The ends were closed by light traps, the baffle boards of which were inclined in the direction of flow of the water as shown in Fig. 3. The lids were light-tight. All holes and cracks were closed with pitch and the whole interior was painted a dead black.

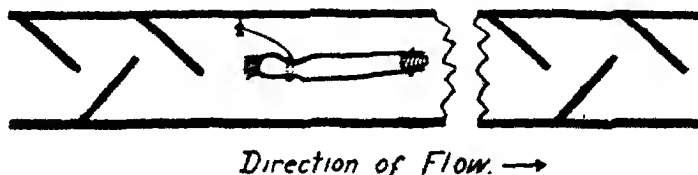


Fig. 3.

The boxes were weighted so as just to float; the waves washed entirely over them except when the water was perfectly quiet. They were anchored in the bay (Friday Harbor, Wash.), where the tidal currents are heavy so that at almost all hours of the day there was a flow of water through them. They were large enough to hold several specimens without materially impeding the flow of water.

In the first experiment the top foot and a half of stipe from the kelp was filled with air by displacement, as previously described, then corked and placed in sea water in the dark boxes, the fronds being removed from half of them. After 5 days in the dark the gas was analyzed. All specimens showed carbon monoxide. The range was from 0.4 to 1.7% with an average of 0.7% of carbon monoxide. The 20.9% of oxygen in the air with which they had been originally filled had practically disappeared and there was about 4% of carbon dioxide. The oxygen was, no doubt, used by respiration and decay processes.

This data was checked by repeated similar series of experiments and it was made certain that in the dark as well as in the light carbon monoxide was formed regularly in the air-filled sections of the stipe, and that there was no relation between its appearance and the presence or absence of the fronds.

An analogous appearance of carbon dioxide and lowering of the oxygen content was shown when un mutilated plants were kept for some time in the dark. The experiment and results are as follows: Twelve whole plants were carefully collected from the same bed. Precautions were taken to avoid in any way disrupting the gas cavity. The gas from 6

of them was analyzed at once and showed an average of 15% of oxygen, 3.2% of carbon monoxide and no carbon dioxide, the unabsorbed residue being nitrogen. The 6 other plants were placed intact in the dark boxes and after being anchored out in the tidal currents for 6 days showed the following average gas composition. Oxygen 4.7%, carbon monoxide 2.9%, and carbon dioxide 0.5%. There was thus a marked decrease in the oxygen content, an appearance of carbon dioxide, which is not present in the plants when freshly collected, while the carbon monoxide content was practically unaltered. These changes in the oxygen and carbon dioxide content produced by stopping photosynthetic action for a prolonged period throws interesting side-lights on the gas exchange equilibria within the living plant. The formation of the carbon dioxide on protracted standing in the dark shows that gaseous respiration products certainly do find their way into the interior cavity of the plant. Whether or not these gases bear only an incidental relation to the metabolic processes of the kelp has not been determined but should prove a fruitful field for research.

The substitution of gases other than air for those normally present was next undertaken.

As a result of more than 40 carefully executed experiments, in which nitrogen was substituted for the kelp gas, it can be confidently stated that *no carbon monoxide was formed*, either in the light or in the dark, either when the fronds were present or when they had been removed, or at any intermediate time between the initial filling with nitrogen and the 8 to 10 days that elapsed before decay had become so pronounced that observation could no longer be made. It should be remarked that carbon dioxide was formed to the extent of several per cent., even though there was no oxygen present.

Nitrogen prepared by 3 different methods was used. First, by heating ammonium chloride and potassium nitrite, then washing through alkali and then conc. sulfuric acid. Second, from air by absorbing the oxygen in alkaline pyrogallol. Third, the commercial product obtained from the distillation of liquid air. This last contained a little more than a half of one per cent. of oxygen. The character of results was the same for the nitrogen, irrespective of the source.

Similar experiments were carried out in which hydrogen was substituted for kelp gas. The 15 determinations made showed no formation of carbon monoxide within 5 to 7 days, either in the light or in the dark. Here as in the case of the nitrogen-filled kelp several per cent. (1% to 9%) of carbon dioxide was formed. It should be remarked that there was always a marked reduction in pressure for hydrogen filled kelp. This amounts to an absorption or an outward diffusion of the hydrogen. The

whole relation of hydrogen in this connection deserves a more exhaustive study.

The hydrogen used was from two sources: first, the action of dil. sulfuric acid on the so-called arsenic-free zinc, and, second, electrolytic hydrogen.

A number of sections of kelp stipe were filled with a mixture of nitrogen and oxygen. The gas was 15.2% oxygen and the remainder nitrogen. After 6 days' anchoring out in the sea water carbon monoxide had formed in all cases, the quantities ranging from 0.8% to 2.1%. The oxygen content had decreased and some carbon dioxide was formed just as in the case of the kelp that had been filled with air. Similar results were obtained when a mixture of hydrogen and oxygen was substituted for the gas originally present in the kelp.

The kelp withstands exposure very well and can remain hours or even days out of water and will resume normal activity when returned to the sea, that is, if not too severely sun burned or desiccated. Tightly corked air-filled sections of stipe were found to produce carbon monoxide, either in the light or in the dark, when simply exposed to the air. These plants were still alive, although local decay soon set in. When the substituted gas was nitrogen or hydrogen no carbon monoxide was formed. It appeared only when free oxygen was within the gas cavity.

That the formation of carbon monoxide takes place only within the living plant was shown by its complete failure to be formed in the air-filled stipes of kelp that had been killed. Some of the plants were killed by immersion for 10 minutes in sea water at 50°; others by being placed in 0.02 N copper sulfate solution for 18 hours. These filled with air or other gas mixtures containing oxygen failed to produce carbon monoxide whether in the sea water or exposed dry to the air.

Conclusions.

The several per cent. of free carbon monoxide which occurs in the floater of the giant Pacific Coast kelp, *Nereocystis leukeana*, is considered to be a respiration product for the following reasons: It forms only when oxygen is present within the floater; it forms as readily in the dark as in the light; is not formed by enzyme or fermentation process when the substance of the plant undergoes autolysis and decay, and is not formed in killed plants.

The kelp, *Nereocystis leukeana*, seemed to be remarkably well adapted to research on the gas exchange of living cells. By the use of the very refined methods of gas analysis some very interesting and valuable information might be gained as to the mechanism of plant processes. It is possible that traces of hydrogen, carbon monoxide, or other gases, not revealed by the technical analytical methods used in this work may be playing unsuspected and perhaps important roles in plant processes.

Conditions have now arisen which make it highly improbable that either

the present authors will pursue this investigation farther, and it is with some regret that we leave this field to other workers.

This research was carried out during the summer of 1917 at the Puget Sound Marine Station, at which time the authors were associated with the University of Washington.

Summary.

1. The existence of several per cent. of carbon monoxide in the gas contained in the Pacific Coast kelp, *Nereocystis luetkeana*, is confirmed.
2. The substance of the kelp, when ground and allowed to undergo autolysis and decay does not form carbon monoxide by enzyme action or fermentation process.
3. Kelp plants, in which the gas normally present within the floater is replaced by air, form several per cent. of carbon monoxide within a few days.
4. The formation of carbon monoxide takes place only when oxygen is present as one of the gases within the floater. No carbon monoxide is formed when the floater is filled with hydrogen or nitrogen.
5. Light does not affect the rate of formation of carbon monoxide.
6. It is concluded that the carbon monoxide is formed as a product of respiration rather than as a intermediate step in photosynthesis.

EVANSTON, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]
**A COMPARISON OF THE ACTIVITY OF CERTAIN UNSATURATED
GROUPS WITH THE ACTIVITY OF THE ALLYL
GROUP IN CERTAIN ETHERS.¹**

By S. G. POWELL WITH ROGER ADAMS

Received January 7, 1920

It has long been an established fact that the allyl group is bound only very loosely to oxygen, nitrogen, sulfur, or halogen. As examples of the mobility of the allyl group may be mentioned the ease of rearrangement of allyl thiocyanate to allyl isothiocyanate,² the great reactivity of allyl halides,³ the readiness with which the allyl group is eliminated from certain nitrogen compounds⁴ and the rearrangement of O-allyl acetoacetic ester or O-allyl acetylacetone⁵ into the corresponding C-substituted compounds. The most striking example, however, is the quantitative

¹ This communication is an abstract of work done by S. G. Powell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² *Ber.*, 8, 464 (1875); *Ann.*, 178, 89 (1875).

³ *J. Chem. Soc.*, 97, 416 (1910).

⁴ *Ibid.*, 57, 767 (1890); 104, 39 (1913); *Ann.*, 382, 1 (1911); *Ber.*, 33, 1438, 2728 (1900).

⁵ *Ber.*, 45, 3157 (1912).

rearrangement of allyl phenyl ethers into *o*-allyl phenols.¹ This reaction has already proved itself to be a most useful one and has invited the attention of many investigators.² A theoretical explanation, however, of the activity of the allyl group has never been given.

The object of this research was to explain the phenomenal mobility of the allyl group. As the first point of attack, a determination of the exact structure which leads to such activity was undertaken and the results are described in this communication. The investigation was started by comparing other unsaturated groups with the allyl for the purpose of discovering (1) whether a C = in any other position besides the $\beta\gamma$, and (2) whether any other unsaturated linkage in the $\beta\gamma$ position, would be just as effective in producing a mobile group as a C=C in the same position. Since the rearrangement of the allyl phenyl ethers to *o*-allyl phenols merely by heating to the boiling point for a short time is such an extremely smooth reaction, the rearrangement of other unsaturated phenyl ethers was attempted. The results of this work have shown that none of the following ethers rearranges under the same conditions as the allyl phenyl ethers: $\text{ROCH}=\text{CH}_2$, $\text{ROCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, $\text{ROCH}_2\text{C}\equiv\text{CH}$, ROCH_2CN , ROCH_2R ; where R stands for a phenyl or substituted phenyl group.

In a German patent³ covering allyl phenyl ether rearrangements, it is stated that the compounds, $\text{ROCH}=\text{CH}_2$, $\text{ROCH}(\text{C}_6\text{H}_5)_2$, rearrange, but no experimental details are given. It is likely that these statements were made in anticipation of what might take place, as the results of this work indicate no rearrangement in these compounds. When phenyl vinyl ether was refluxed for 12 hours there was no change. When this substance was heated in a sealed tube for 12 hours at $260\text{--}280^\circ$, there was only very slight decomposition with the formation of phenol. The *p*-tolyl-vinyl ether, upon heating in a sealed tube to 230° did, to be sure, decompose, but the chief reaction product was *p*-cresol. Moreover, heating the same compound for 2 hours at its boiling point (177°) yielded chiefly *p*-cresol along with tarry products.

The 3 substances, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{C}\equiv\text{C}(\text{CH}_3)_2$, were next studied. All of them proved to be remarkably stable, for after 12 hours refluxing neither rearrangement nor decomposition had taken place.

On the other hand, phenyl-propargyl ether and *p*-bromophenyl-propargyl ether were found to be very unstable. Refluxing brought about complete decomposition within 2-3 hours, giving tarry mixtures in

¹ *Ann.*, 401, 21 (1913); 418, 69 (1919).

² *Ber.*, 48, 1716 (1915); *THIS JOURNAL*, 39, 2202 (1917); 41, 654 (1919); *Ann.*, 414, 250 (1918).

³ *D. R. P.* 268,090, *Frdl.*, 11, 181 (1912-14).

each case. Even in amyl ether (b. p. 170°) as a solvent, extensive decomposition took place. In none of the rearrangement experiments was alkali soluble material found.

Of the ethers with a $C\equiv N$ linkage in the $\beta\gamma$ position, the following were chosen for study: $C_6H_5OCH_2CN$ and $p\text{-CH}_3C_6H_4OCH_2CN$. Although the former showed some decomposition, after 15 hours refluxing, the latter upon 24 hours heating set to a solid brittle tar. When amyl ether was used as a solvent, very little decomposition occurred, a small amount of *p*-cresol being obtained.

Finally, the benzyl ethers were investigated, and as they are very similar in structure to the allyl ethers, the expectation was that they would rearrange. Of these, benzyl phenyl ether, benzyl tolyl ether, and several of their nitro and bromo substitution products were studied. In no case did rearrangement take place. It was found that undoubtedly the linkage between the benzyl group and the oxygen is a weak one, but the chief products of the decomposition are not diphenylmethane, but benzene and toluene derivatives. The nitro compounds in general decompose rapidly and the bromine derivatives break down completely with the evolution of hydrobromic acid.

In connection with the study of the benzyl ethers, it is interesting to note the results which have been obtained by previous investigators on the comparative ease with which the benzyl and allyl compounds decompose or react. Clarke¹ has found by a study of the reaction between various bromides and pyridine that benzyl bromide is nearly 5 times as active as allyl bromide. On the other hand, von Braun² studying the quaternary ammonium halides discovered that in every case allyl chloride would split off in preference to benzyl chloride and both of them far more easily than alkyl or aryl chlorides. Thus it is obvious that in certain reactions the benzyl is more reactive than the allyl and in other cases less reactive. No definite results on this point were obtained by a study of the phenyl ethers.

In conclusion, the rearrangement of phenyl ethers is not a suitable reaction for the study of the comparative reactivity of various unsaturated groups. It is possible that satisfactory results can be obtained by a study of the rearrangements of derivatives of O-acetoacetic ester to C-acetoacetic ester or of the decomposition of the quaternary ammonium halides as investigated by von Braun. It is even possible that the rearrangements of the thiocyanates to isothiocyanates is a field in which various unsaturated groups may be compared.

Experimental.

Phenyl-Vinyl Ether, $C_6H_5OCH=CH_2$.—This substance was prepared by the action of solid sodium hydroxide upon phenyl- β -bromo-

¹ *J. Chem. Soc.*, 97, 416 (1910).

² *Ber.*, 33, 2438, 2728 (1900); *Ann.*, 382, 1 (1911).

ethyl ether.¹ It boils at 155–156°. Twenty g. of this product was refluxed for 12 hours and then distilled. No decomposition had taken place. In a second experiment, 20 g. was heated in a sealed tube at 260–280° for 12 hours. The product took on a light brown color. On distilling, most of the product boiled at 155–165° and was without question unchanged ether; a small lower fraction, less than one g., had a strong, piercing odor but was not identified, while a high boiling fraction of about 4 g. was shown to be phenol.

***p*-Tolyl-Vinyl Ether**, $\text{CH}_3\text{C}_6\text{H}_4\text{OCH}=\text{CH}_2$.—This substance was made in a similar manner to the phenyl vinyl ether using *p* cresol in place of phenol. The intermediate *p* tolyl β bromoethyl ether² has already been described and is a colorless crystalline solid melting at 40° and boiling at 254–255°. To prepare the vinyl ether, 100 g. of the bromo compound is mixed with 200 g. of powdered sodium hydroxide in a 500 cc. copper flask and distilled from an oil bath at 250–300°. The distillate is extracted with a small amount of ether, the ether solution dried over sodium sulfate, and then fractionated. The *p*-tolyl-vinyl ether is a colorless, mobile liquid with a pleasant odor, b. p. 177–180°, n_D^{20} 1.513, D_4^{20} 0.975.

Subs., 0.2504: CO_2 , 0.7370, H_2O , 0.1620

Calc. for $\text{C}_9\text{H}_{10}\text{O}$: C, 80.6; H, 7.5. Found: C, 80.3; H, 7.2

Twenty g. of this substance was heated for 10 hours in a sealed tube at 230°. Upon cooling the product was a dark reddish brown, tarry substance which was dissolved in ether and this solution then extracted with 10% sodium hydroxide solution. It was found that the alkali contained a considerable portion of *p*-cresol. The alkali insoluble products were tarry in nature and no definite substance could be obtained from them. Even upon merely refluxing for 2 hours, the *p*-tolyl vinyl ether decomposed to give *p*-cresol and high boiling, dark colored, alkali-insoluble material.

An attempt was made to prepare the *p*-bromophenyl-vinyl ether first by the action of alkali upon the *p*-bromophenyl β -bromoethyl ether,³ and second by the decomposition of β -*p*-bromophenoxy-ethyl-trimethyl ammonium bromide. Neither of these methods gave the product that was desired. The *p*-bromophenyl- β -bromoethyl ether gave deep-seated decomposition upon heating with alkali.

β -*p*-Bromophenoxy-ethyl-trimethyl Ammonium Bromide, $\text{BrC}_6\text{H}_4\text{-OCH}_2\text{CH}_2(\text{CH}_3)_3\text{NBr}$.—This substance is formed by heating 56 g. of *p*-bromophenyl- β -bromoethyl ether in a sealed tube at 100° for 12 hours with excess of a methyl alcohol solution of trimethylamine. Upon

¹ *Ber.*, 43, 2178 (1900).

² *Ibid.*, 24, 189 (1891).

³ *J. Biol. Chem.*, 21, 439 (1915).

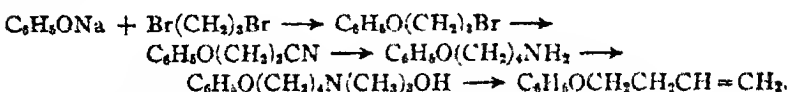
cooling, the contents of the tube are a mass of white crystals which are washed with dry ether to extract unchanged *p*-bromophenyl- β -bromoethyl ether. The quaternary ammonium compound is purified by dissolving in absolute methyl alcohol and reprecipitating with absolute ether.

Subs., 0.9466; 28.5 cc. 0.1 *N* AgNO₃.

Calc. for C₁₁H₁₇ONBr: Br, 23.6. Found: 24.0.

This substance is treated with excess of silver oxide in water solution, the silver bromide filtered and the solution evaporated to a small volume on a water bath. The sirupy residue is then distilled with a free flame but from the distillate no constant boiling fraction is obtained.

Phenoxy-4-Butene-1, C₆H₅OCH₂CH₂CH=CH₂.—This ether has been prepared by the method of Braun¹ by the following series of reactions:



The γ -phenoxypropyl bromide is readily made from the sodium phenylate and trimethylene bromide² and can be obtained in 65% yields. This readily forms the cyanide in 75% yields.³ The nitrile by the action of absolute alcohol and sodium gives 72% yields of amine hydrochloride⁴ which with alkali gives free base. To convert the amine into the quaternary ammonium iodide, then the hydroxide, and finally the ethylene compound, 70 g. is dissolved in one liter of methyl alcohol and mixed with a solution of 75 g. of sodium hydroxide in 200 cc. of water. To this mixture 216 g. of methyl iodide is added slowly. Too rapid addition of the iodide will result in a large portion of the material being thrown out of the top of the condenser. The mixture is refluxed for 8 hours, then allowed to cool when the quaternary ammonium iodide separates out in shining flakes, m. p. 168°. From 77 g. of the quaternary ammonium iodide in 300 cc. of water, and an excess of silver oxide, a solution of the corresponding quaternary ammonium hydroxide is obtained. This is filtered from the silver iodide and evaporated almost to dryness on the water bath, then distilled in a small distilling flask with a free flame. The distillate consists of phenoxy-4-butene-1 and γ -phenoxy-butyl-dimethylamine. By shaking the distillate with ether and then with dil. hydrochloric acid to extract the amine, an ether solution of the ethylene compound is obtained. This is dried over sodium sulfate, the ether removed and the residue fractionated. A colorless liquid, b. p. 209°, is produced.

¹ *Ann.*, 382, 34 (1911); *Ber.*, 44, 3699 (1911).

² *Ber.*, 24, 2631 (1891).

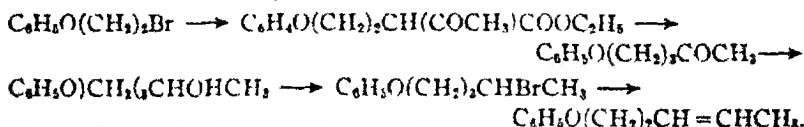
³ *Ibid.*

⁴ *Ibid.*, 24, 3231 (1891); 39, 4119 (1906).

The γ -phenoxy-butyl-dimethylamine may be used over again for the production of the quaternary ammonium iodide.

Twenty g. of phenoxy-4-butene-1 was refluxed for 48 hours. The temperature remained constant at 209° and a distillation showed that no decomposition had taken place. Even after heating in a sealed tube for 5 hours. at $250-270^\circ$ no decomposition took place.

Phenoxy-5-Pentene-2, $C_6H_5OCH_2CH_2CH=CHCH_3$.—This substance has already been prepared by the action of the sodium phenylate upon 1,4-dibromopentane.¹ Since, however, the dibalide is a difficult substance to obtain, a new method was used for the synthesis. This consisted in the following series of reactions



Phenyl- β -bromoethyl ether was prepared by the method described in the literature with slight modifications.² In a 5-liter flask fitted with an upright condenser, 660 g. (3.5 moles) of ethylene dibromide, 280 g. (3 moles) of phenol, and 1000 cc. of water were heated to boiling. To this mixture was added in portions of 25 cc. every half hour 500 cc. of 4 *N* sodium hydroxide solution (2 moles); after all the alkali had been added, the mixture was heated 2 hours longer. Upon cooling, the lower oily layer was separated, washed with dil. sodium hydroxide solution and distilled. As soon as the ethylene dibromide had come over, the remainder of the material was distilled under diminished pressure and the fraction boiling $130-145^\circ$ at 25 mm. collected. It solidified to a mass of white crystals, m. p. 33° , and amounted to 225 g. (55% yield). The bromide was next condensed with sodium acetoacetic ester and the resulting compound split to the ketone.³ The ketone was then reduced to the alcohol.

γ -Phenoxy-propyl-methyl Carbinol, $C_6H_5O(CH_2)_3CHOHCH_3$.—A solution of 36 g. of γ -phenoxy-propyl-methyl ketone in 300 cc. of ether is added to 250 g. of sodium hydrogen carbonate mixed with 1000 cc. of water. The whole is cooled with ice and then 60 g. of sodium is added in small portions over a period of 36 hours, keeping the mixture cold at all times. When all of the sodium has been used up, the ether layer is separated, washed with a saturated solution of sodium hydrogen sulfite to

¹ *J. Russ. Phys. Chem. Soc.*, 30, 826 (1898).

² *Ber.*, 43, 2178 (1900).

³ The condensation of phenyl- β -bromoethyl ether with acetoacetic ester and then subsequent decomposition to the corresponding ketone has been carried out in this laboratory in a research under the direction of Dr. Oliver Kamm. The details for the production of these compounds and their physical constants will be published in a communication soon to appear.

remove any unreduced ketone and dried over sodium sulfate. The ether is distilled off on the water bath and the residue fractionated under diminished pressure. The portion boiling $160-165^{\circ}$ at 20 mm. is collected and upon redistillation gives 27 g. (75% yield) of a colorless, viscous oil, boiling at 163° at 20 mm., n_D^{25} 1.5123, D_{25}^{31} 1.025.

Subs., 0.3132, 0.2832; CO_2 , 0.8376, 0.7560, H_2O , 0.2672, 0.2276.

Calc. for $C_{11}H_{16}O$: C, 73.3, H, 8.9. Found: C, 73.0; 72.8; H, 9.5, 8.9

Phenoxy-5-bromo-2-pentane, $C_6H_5O(CH_2)_3CHBrCH_3$.—36 g. of γ -phenoxy-propyl-methyl carbinol is well cooled with ice and treated with 30 g. of phosphorus tribromide. After the addition, the mixture is refluxed for 30 min. to complete the reaction and then poured into ice water. The oily layer is taken up with ether, the ether solution washed with dil. sodium hydroxide, then with water and finally dried over sodium sulfate. The ether is distilled off on the water bath and the residue fractionated under diminished pressure. The crude fraction distilling at $165-70^{\circ}$ at 25 mm. is redistilled and yields 36 g. (75% yield) of a colorless oil boiling at 172° at 28 mm., n_D^{30} 1.529, D_{25}^{30} 1.258

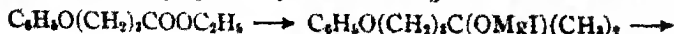
Subs., 0.2766, AgBr, 0.2093

Calc. for $C_{10}H_{15}OBr$: Br, 32.9. Found 32.2

Phenoxy-5-pentene-2, $C_6H_5OCH_2CH_2CH=CHCH_3$.—A mixture of 30 g. of phenoxy-5-bromo-2-pentane and 200 cc. of a 10% alcoholic potassium hydroxide solution is refluxed for 10 hours. At the end of this time the mixture is poured into water, the oil separated and taken up in ether. The ether is dried, distilled and the residue fractionated under diminished pressure. The crude fraction from $122-130^{\circ}$ at 25 mm. on redistillation gives 14 g. (70% yield) of a colorless oil boiling 132° at 32 mm., n_D^{30} 1.5005, D_{25}^{31} 0.957. At ordinary pressures the substance boils at 226° .

Twenty g. of this ether was heated to boiling for 12 hours. The boiling point remained absolutely constant during the whole time and upon distillation at the end of this period showed that no decomposition had taken place.

Phenoxy-5-methyl-2-pentene-2, $C_6H_5O(CH_2)_3CH=C(CH_3)_2$.—This substance was prepared by the following series of reactions:



Ethyl- γ -phenoxy-butyrate, $C_6H_5O(CH_2)_3COOC_2H_5$.—The γ -phenoxy-butyric acid was obtained by the acid hydrolysis of β -phenoxy-ethyl malonic ester.¹ A solution of 90 g. (5 moles) of γ -phenoxy-butyric acid in 500 cc. of absolute alcohol is saturated with dry hydrogen chloride and refluxed for 2 hours. Upon cooling, the reaction mixture is diluted with

¹ Ber., 44, 1507 (1911).

water, extracted with ether, the ether solution washed with dil. sodium carbonate solution, then with water and finally dried over sodium sulfate. Upon removal of the ether, the residue is fractionated under diminished pressure and the crude material boiling at $165\text{--}180^\circ$ at 25 mm. fractionated. The pure ester boils at $170\text{--}173^\circ$ at 25 mm., n_D^{25} 1.491, D_4^{25} 1.048.

Subs., 0.2834; CO_2 , 0.7200; H_2O , 0.1984

Calc. for $\text{C}_{12}\text{H}_{16}\text{O}_4$ C, 69.2, H, 7.7 Found. C, 69.3, H, 7.8

This same ester may be even more conveniently prepared by the action of alcohol and sulfuric acid upon γ -phenoxy-butyronitrile.¹ A mixture of 90 g. of the nitrile, 300 cc. of absolute alcohol, 100 cc. of conc. sulfuric acid is refluxed for 5 hours; upon cooling the mixture is diluted with ice and water and extracted with ether. Upon drying with sodium sulfate, distilling the ether and fractionating the residue under diminished pressure, the ester is obtained with the same boiling point described above.

Phenoxy-5-methyl-2-pentene-2, $\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_2\text{CH}=\text{C}(\text{CH}_3)_2$.—A suspension of 27 g. of magnesium in 400 cc. of dry ether is treated with 160 g. of methyl iodide. The Grignard solution is then added drop by drop to a well-cooled solution of 104 g. of ethyl- γ -phenoxy-butyrate in 300 cc. of dry ether. After all has been added, the mixture is allowed to stand overnight at room temperature. It is then poured on ice, acidified with hydrochloric acid, the ether layer removed, washed with a little sodium hydrogen sulfite to remove traces of iodine, dried over sodium sulfate. After removal of the ether, the residue is fractionated and 2 main portions are obtained, the larger one boiling at $137\text{--}8^\circ$ at 25 mm. and the smaller boiling at $166\text{--}167^\circ$ at 20 mm. This lower fraction is the compound desired. It boils at 241° at 745 mm., n_D^{20} 1.505. The higher boiling fraction was not identified.

Subs., 0.2548; CO_2 , 0.7584; H_2O , 0.2114.

Calc. for $\text{C}_{12}\text{H}_{16}\text{O}$ C, 81.8; H, 9.1. Found. C, 81.2; H, 9.2.

Twenty g. of the ether was refluxed for 12 hours. The temperature remained constant throughout this period and upon distillation at the end there was no indication that any decomposition had taken place.

Phenyl-propargyl Ether, $\text{C}_6\text{H}_5\text{OCH}_2\text{C}\equiv\text{CH}$.—This substance has already been prepared by the action of alcoholic potash upon phenyl- β -bromo-allyl ether² and the phenyl- β -bromo-allyl ether has been formed by the action of sodium phenylate upon β -bromo-allyl bromide. In this research, however, it was found that phenyl- β -bromo-allyl ether is much more readily formed by the action of sodium phenylate upon tribromohydrin.

Phenyl- β -bromo-allyl ether, $\text{C}_6\text{H}_5\text{OCH}_2\text{CBr}=\text{CH}_2$.—In 300 cc. of absolute alcohol 24 g. of sodium is dissolved and then 94 g. of phenol added

¹ Ber., 24, 2632 (1891).

² Bull. soc. chim., 40, 324 (1883).

to the hot solution. To this mixture 135 g. of tribromohydrin is gradually added. A very vigorous reaction takes place immediately with a copious precipitate of sodium bromide. The alcohol is now distilled off from the water bath, the residue diluted with water, extracted with ether, the ether extract washed with dil. sodium hydroxide solution, and then dried over sodium sulfate. After removal of the ether, the residue is distilled under diminished pressure and the fraction boiling 125–135° at 25 mm. redistilled. It boils practically constant at 135° at 30 mm. and amounts to 84 g. (83% yield).

The formation of the phenyl-propargyl ether from this bromo compound was carried out exactly as described by Henry.¹ When pure, it boils 111–112° at 40 mm. and at atmospheric pressure 209°. The yield is about 53%.

When 20 g. of phenyl-propargyl ether was heated to boiling under a reflux condenser for 5 hours and then allowed to cool, a solid black tar was produced from which no definite substance could be isolated. It was apparent that the ether had completely decomposed. A second experiment was made, refluxing the phenyl-propargyl ether in di-isoamyl ether (b. p. 170°) for 100 hours. Soon after the heating was started, a dark brown solid began to separate out. At the end of the period indicated, the phenyl-propargyl ether was apparently completely decomposed. When the reaction was carried on in exactly the same way but the refluxing continued for 20 hours only, the same tar was obtained but at least $\frac{2}{3}$ of the phenyl-propargyl ether remained unchanged. In none of the experiments was alkali soluble material obtained.

p-Bromophenyl-propargyl Ether, $\text{BrC}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{CH}$.—This substance was formed by the action of alcoholic potash upon the *p* bromophenyl- β -bromo-allyl ether which in turn was produced by the action of excess of sodium *p*-bromophenylate upon tribromohydrin.

p-Bromophenyl- β -bromo-allyl ether $\text{BrC}_6\text{H}_4\text{OCH}_2\text{CBr}=\text{CH}_2$.—The details for the preparation of this substance are the same as those described under the preparation of phenyl- β -bromo-allyl ether. The substance boils at 171° at 22 mm., n_D^{22} 1.587, D_4^{22} 1.719.

Subs., 0.3852, 0.2402; AgBr, 0.4928, 0.3054.

Calc. for $\text{C}_6\text{H}_5\text{OBr}$, Br 54.7. Found: 54.1, 54.4.

p-Bromophenyl-propargyl ether, $\text{BrC}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{CH}$.—The details for the preparation of this ether from the bromo compound just described are just the same as those used in the preparation of the corresponding phenyl ether. The product is obtained in 50% yields, boils at 144° at 24 mm., n_D^{30} 1.567, D_4^{30} 1.468.

Subs., 0.3688, 0.3942; AgBr, 0.3377, 0.3609.

Calc. for $\text{C}_6\text{H}_5\text{OBr}$, Br, 54.0. Found: 59.0, 59.0.

¹ Bull. soc. chim., 40, 324 (1883).

Upon refluxing 20 g. of *p*-bromophenyl-propargyl ether, the temperature gradually rose during the course of 30 minutes from 254—266°. Upon cooling the mass set to brittle tar indicating almost complete carbonization. A second experiment was carried out using di-isoamyl ether as a solvent and the solution was heated for 10 hours. Partial decomposition took place but no alkali soluble product was produced.

Phenoxy-acetonitrile, $C_6H_5OCH_2CN$.—This substance has been prepared by the following series of reactions:



The directions described in the literature were followed.¹ The dehydration of the amide, however, was varied so that a better yield could be obtained. The following procedure is very satisfactory.

Phenoxy-acetonitrile, $C_6H_5OCH_2CN$.—75 g. of dry phenoxy-acetamide is placed in a 500 cc. distilling flask and melted. Into this is now poured directly 60 g. of phosphorus pentoxide and the mixture distilled as rapidly as possible. The distillate, containing both nitrile and unchanged amide, is treated with dry ether which dissolves the nitrile but not the amide, so that the latter may be filtered off. Upon distillation of the ether and vacuum distillation of the residue the nitrile is obtained as a colorless oil boiling at 132° at 30 mm. or 235° at 745 mm.

25 g. of phenoxy-acetonitrile upon refluxing 15 hours turned red and finally black, but the temperature remained constant at about 240°. At the end of this time, distillation showed that practically 90% of the material was unchanged.

***p*-Methyl-phenoxy-acetonitrile**, $CH_3C_6H_4OCH_2CN$.—This substance was prepared from *p*-cresol by the same series of reactions used for the preparation of phenoxy-acetonitrile. This method of preparation has not previously been used, but since the details for the various steps are identical with those employed in the same series of reactions using phenol, they are not given here.¹ The *p*-methyl-phenoxy-acetic acid² thus obtained melted at 135°. By esterification the ethyl-*p*-methyl-phenoxy-acetate was formed and proved to be a pleasantly smelling liquid boiling at 266–267° at 740 mm. which is quite different from the constants for this compound as described in the literature.³ It has previously been made from sodium *p*-cresylate and ethyl chloroacetate and the boiling point given was 243° at 752 mm. A sample prepared according to this method gave identically the same boiling point as was obtained by the above method, the esterification of the corresponding acid. The amide⁴ forms

¹ *J. prakt. Chem.*, [2] 20, 275 (1897).

² *Ber.*, 24, 923 (1891).

³ *J. Chem. Soc.*, 103, 1630 (1913).

⁴ *Gazz. chim. Ital.*, 22, II, 525 (1892).

from the ester readily by the action of aqueous ammonia at room temperature and the nitrile from the amide by the action of phosphorus pentoxide. The nitrile as obtained was a colorless, pleasantly smelling oil boiling at 148–149° at 28 mm. and upon cooling gave white crystals melting at 40°. These constants correspond to those obtained by Stoermer, for the substance as prepared by the dehydration of *p*-methyl-phenoxy-acetaldoxim.¹

Upon refluxing *p*-methyl-phenoxy-acetonitrile for 24 hours and then allowing to cool, the entire contents of the flask set to a brittle tar, indicating complete decomposition. When refluxed for 15 hours in di-isoamyl ether as a solvent, the larger part of the product proved to be unchanged nitrile; a few grams, however, of a fraction soluble in alkali proved to be *p*-cresol. A repetition of this last reaction but boiling for 90 hours gave practically the same results.

An attempt was made to prepare the *p*-bromo-phenoxy-acetonitrile but it was found impossible to dehydrate the amide without deep-seated decomposition, so that no pure nitrile was obtained. The ethyl-*p*-bromo-phenoxy-acetate was made from an alcoholic solution of sodium *p*-bromophenylate and chloroacetic ester rather than by the bromination of ethyl-phenoxy-acetate as is described in the literature.² The physical constants were the same in both cases. They form white crystals, m. p. 59°.

p-Bromo-phenoxy-acetamide, $\text{BrC}_6\text{H}_4\text{OCH}_2\text{CONH}_2$.—A solution of 130 g. of ethyl-*p*-bromo-phenoxy-acetate in one liter of 80% alcohol is made and then saturated with ammonia gas at 0°. After standing 24 hours a large proportion of the amide crystallizes out in long colorless needles. The solid is filtered off and by concentrating the mother liquors, more amide is obtained. To purify, it is crystallized from dilute alcohol, m. p. 148–9°.

Subs., 0.2850; 17.3 cc. 0.0714 *N* HCl.

Calc for $\text{C}_8\text{H}_8\text{O}_2\text{NBr}$. N, 6.1. Found 6.1.

A series of phenyl-benzyl ethers was made by the action of benzyl chloride or bromide, or substituted benzyl chloride or bromide upon phenol or a substituted phenol in the presence of potassium carbonate and acetone as a solvent.

Phenyl-benzyl ether, $\text{C}_6\text{H}_5\text{OCH}_2\text{C}_6\text{H}_5$.—A mixture of 126 g. (one mole) of benzyl chloride, 105 g. (1.1 mole) of phenol, 138 g. of potassium carbonate and 100 cc. of acetone is refluxed for 8 hours. After dilution with water, the benzyl-phenyl ether is taken up in ether, the ether solution washed with aqueous alkali and dried over sodium sulfate. After removing the ether the benzyl-phenyl ether is distilled under diminished pressure. It boils at 178–79° at 35 mm. and melts at 39°.³

Upon refluxing 100 g. of this ether for 4 hours, the temperature of the

¹ Ber., 30, 1700 (1897).

² J. prakt. Chem., [2] 20, 275 (1897).

³ Ann., 217, 43 (1883).

liquid dropped rapidly from 272° to 220° . The contents of the flask was a dark red liquid which was taken up with ether and the ether solution extracted with dil. potassium hydroxide solution. Upon investigation of the alkaline solution it was found that a considerable quantity of phenol was present. The alkali insoluble material contained toluene, unchanged benzyl-phenyl ether and a small amount of a high-boiling product which was not identified.

The following benzyl ethers were also prepared:

	This communication M p	In literature. M p.
<i>p</i> -Bromophenyl-benzyl ether	b ₃₀ 226° 64°	b ₃₀ 226° 1
<i>p</i> -Nitrobenzyl-phenyl ether	91°	91° 2
<i>p</i> -Nitrobenzyl- <i>o</i> -tolyl ether	90°	90° 3
<i>p</i> -Nitrobenzyl <i>p</i> -tolyl ether	89°	89° 3
<i>p</i> -Nitrobenzyl- <i>p</i> -methoxy-phenyl ether Yellow needles from alc	88°	
Subs., 0.5352, 26.0 cc N, 747 mm and 48° Calc for $C_{14}H_{13}O_2N$ N, 5.4 Found 5.4		
<i>p</i> -Nitrobenzyl- <i>p</i> -bromophenyl ether Yellow needles from alc	112°	
Subs., 0.4416, AgBr, 0.2684 Calc for $C_{14}H_{11}O_2NBr$ Br, 25.97 Found 25.86		
<i>p</i> -Nitrobenzyl-2,4-dibromo phenyl ether Yellow needles from alc	161°	
Subs., 0.3862, AgBr, 0.3706 Calc for $C_{14}H_9O_2NBr_2$ Br, 41.34 Found 40.83		
<i>p</i> -Bromobenzyl <i>p</i> -bromophenyl ether	111°	111° 4
<i>p</i> -Bromobenzyl-2,4-dibromo phenyl ether	100°	100° 4

The nitro compounds described above when heated to their boiling point gave deep seated decomposition. Even at lower temperatures, decomposition took place although more slowly. No definite products could be isolated.

The halogenated ethers evolve hydrobromic acid when heated to the boiling point and give in general a certain amount of phenol or substituted phenol and a little toluene or substituted toluene. In every instance complete decomposition took place.

Summary.

1. The preparation of several ethers of each of the following types has been carried out: $ROCH=CH_2$; $ROCH_2CH_2CH=CH_2$; $ROCH_2C\equiv CH$; $ROCH_2CN$; $ROCH_2R$; where R stands for phenyl or substituted phenyl group.

2. A comparison of the stability of these ethers upon heating has been made with the corresponding allyl-phenyl ethers.

¹ *Ann.*, 357, 90 (1907)

² *Ibid.*, 224, 104 (1884); *THIS JOURNAL*, 39, 309 (1917).

³ *Ibid.*, 39, 309 (1917).

⁴ *Ann.*, 357, 90 (1907).

3. It has been found that none of these compounds rearranges into substituted phenols in a manner similar to the allyl-phenyl ethers.

URBANA, ILLINOIS.

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, SOUTH DAKOTA STATE COLLEGE OF AGRICULTURE AND MECHANIC ARTS.]

PROSO MILLET INVESTIGATIONS—ANALYSIS OF THE OIL—A CHARACTERISTIC ALCOHOL.

By B. A. DUNBAR AND E. R. BINNEWIES.

Received January 10, 1920

While engaged in an exhaustive examination of the grain of the proso millet, with a view to its employment as a commercial food source, certain peculiarities of the ether extract from the finely divided grain came to our attention. These unusual features led to the following series of investigations, which, while as yet open to further work, have brought out several interesting details, when viewed from the standpoint of the cereal analyst.

This variety of millet, termed *proso* from the Russian name for the "true millet," was denominated by Linnæus, *panicum miliacum*. It is extensively cultivated in the region of the Altai Mountains in Siberia, in Southern Russia, and in the semi-arid areas of eastern and southern Asia, where it constitutes a staple foodstuff for both man and the lower animals. Its botanical name suggests its productivity, which is marked, even in regions where other common grains do not thrive by reason of aridity of climate. Our first undertaking was merely one involving the analysis of the grain to determine its nutritive factors and, particularly, its gluten and gliadin content, as affecting its adaptability as a bread-stuff, and so to throw light upon its possibilities as a food crop for our semi-arid regions west of the Missouri River.

The grain upon which we undertook our studies was raised upon the farms of this institution, from specially selected white seed derived by selection from mother seed obtained in Russia by Professor N. E. Hansen, of this college. Two analyses were made upon the seed, the first upon a coarsely ground meal, unbolted, and the second upon bolted flour from the same grade of grain. The former sample consisted of the hulled grain, ground to pass through a 70-mesh sieve but without further treatment. In the second case, the grain, hulled and pulverized, was passed through the ordinary No. 60 mill screen, so producing a flour similar in fineness to the so-called "Red Dog" grade of wheat flour. By this process, the crude fiber content was materially reduced and the percentage of starch was largely increased, as compared with like data from the coarser samples first taken from the unbolted meal. The following table is presented to show in percentages the analytical results from

unbolted meal, bolted flour, and an average comparable analysis of patent wheat flour, according to Leach's tables.¹

	Ash	Mela- ture.	Cr. Fib.	Cr. Prot.	Eth Extr	N- Free.	Starch.	Total.
Proso meal.....	2.86	12.80	6.25	15.86	5.07	57.16	59.65	100.00
Proso flour bolted.....	1.45	10.09	0.80	14.90	3.32	69.44	69.15	100.00
Patent wheat flour.....	0.44	12.77	0.21	10.55	1.02	74.90	...	99.89

According to the above data, we note that aside from the inferences which our original problem led us to form as to the food value of the grain, its oil content is low as compared with that of many other common oil-bearing seeds now in use as oil sources of commercial moment, but it was found that, by extraction of the coarser material for a 16-hour period, we could depend upon a constant 5% extract, and we have used such means in obtaining the quantity of oil needed for our special work upon the oil.

To prepare the oil for this work, we proceeded as follows. The selected hulled seed was ground through a common laboratory hand mill, keeping the crushers tight. The product passed through a 40-mesh sieve. This meal was extracted in a specially constructed apparatus, consisting essentially of a large glass cylinder, constricted at both ends, about 125 cm. in length, and surmounted by a Liebig condenser in position for refluxing. The cylinder was furnished with an inner tube which passed from a point below the lower end of the cylinder, through a cork inserted in this end, up through the meal to be extracted and above the surface of the charge, which consisted of about 18 kg. of meal. Between the cork stopper, which was perforated with small glass tubes to permit egress of oil-saturated ether, and the charge was placed a 2-inch layer of glass wool. An aluminum cone was suspended from the lower end of the reflux condenser, to distribute the return flow of condensed ether. The whole was connected, as usual, with a boiling flask of 2 liters capacity and the extraction continued for 16 hours per charge. As the quantity of oil sought for the work precluded the use of expensive ethyl ether, we made use of petroleum ether, which we found, upon trial, to be almost as efficient as anhydrous ether both in point of amount of yield of oil, and in quality of the product. The extraction was considered to be complete when the medium issued from the cylinder practically water-white and left but the slightest trace of oil upon evaporation of 50 cc. The oil so extracted, upon distilling off the solvent, was at first of a medium straw color, changing, upon standing, to a light golden yellow, the oil being quite mobile, with an odor distinctly characteristic of this product. The oil, so extracted, was the subject of the following experimentation, after filtering out, through coarse linen, a peculiar mass of crystals which

¹ "Food Inspn. and Analysis," 1904, p. 236.

were noticed as collecting in the oil after it had stood out of contact with air for several hours. These crystals were of lustrous appearance, pearly white and in the form of thin plates. After several unsuccessful attempts to separate the oil by the use of solvents, we removed them as mentioned above, washed them free from oil by means of cold ethyl ether, in which the crystals were but very slightly soluble, rewashed them in 95% alcohol, cold, and dried them at 100°, after recrystallization from hot 95% alcohol. The crystal-mass, when so purified, crystallizes in 6-sided pearly plates, closely resembling those of phytosterol, but in other respects markedly differing from the latter, particularly in their melting point, which was sharp at 279°, corrected. These crystals were set aside for further examination, which will be reviewed at a later point in this report.

Physical Characteristics of the Oil.—The oil of proso millet is a semi-drying oil having a specific gravity of 0.9228 at 22.5°, as determined by the pycnometer. It has a refractive index, as determined by the Abbé Refractometer, of 1.4745. These values correspond well with the semi-drying nature of the oil. It is insoluble in 95% alcohol up to 35 volumes and is insoluble in absolute alcohol up to 25 volumes, showing it to be composed very largely of fixed oils, as confirmed by succeeding tests.

Chemical Constants.—The saponification value was 181.5, indicating a possible composition similar to that of peanut oil as to the nature of the acid groups involved, and pointing to its quality as a semi-drying oil. Its iodine value, determined by the Hubl method, was 92.3, showing it to be high in relative amount of unsaturated acids. In point of free fatty acids, the constant was high, corresponding to 119 mg. of oleic acid per g. of oil. This number would, therefore, preclude the use of the oil as a lubricant. The acetyl value was high, 39.23 mg. of potassium hydroxide being required to neutralize the acetic acid produced from hydrolysis of the acetylated fat, per g. This value corresponds, by calculation, to 10.9% of alcohols and hydroxy acids in the original oil, a characteristic of semi-drying oils. The Reichert-Meißl value was fairly large, *vis.*, 2.5. Unsaponifiable matter, as determined by the method of Allen and Thompson, was found to be 2.52 parts per hundred, by weight. It was found to consist of resins, in the main, but in insufficient quantity for exact determination as to type. The elaidin test, conducted according to the method of Andes,¹ gave us, at first, a foamy, orange-yellow, buttery mass, which, after 2 hours, assumed a red-brown and semi-liquid character. These results presume the oil to lie midway between oils like rapeseed, sesame and cottonseed and the more strictly drying oils such as hempseed and linseed. To assure ourselves regarding this point,

¹ "Drying Oils," 1901, 3-4, 574 (1889).

we oxygenated the oil according to the method of Livache,¹ with the following results:

Time of exposure Days	Gain by weight	% of O
1	0	60
2	0	74
3	0	92
4	1	20
5	1	64
6	2	00
7	2	60
14	3	10
21	3	18

These results would rank the oil with the group represented by rapeseed oil, as to its drying properties.

The Lewkowitsch method for determination of crude glycerol,² resulted in a low value, 112, 3.31%. While this small percentage may be partially due to loss through volatility of glycerol in steam during the frequent evaporations involved in the acetin method, such low value was to be expected when the high, free acid value and rather moderate saponification number were taken into consideration.

Phytosterol was determined by the A. O. A. C. method and the product obtained, upon its evaporation and recrystallization from hot alcohol, gave us the characteristic needle tufts to the amount of 0.63% by weight of original oil. Their melting point was 154°, corrected, and their identity so established.

All tests for phenol bodies were negative, and the Schiff test for aldehydes gave but a very faint coloration after the mixture had stood for 2 hours, indicating that aldehydes, if present, are of negligible amount.

As calculated from saponification value, the mean molecular weight of the fatty acids is 296.

Volatile Acids.—56.7 g. of the oil was saponified by alcoholic potash, evaporated to free the soaps from alcohol, the soaps neutralized with excess of sulfuric acid, and warmed to complete the separation of insoluble acids. The acid cake was separated and the residual liquor distilled until distillate gave no reaction with litmus. This distillate was titrated against 0.1 N sodium hydroxide solution and 0.36% of volatile acids found, as calculated to formic acid. A slight acetic acid content was found to form a part of this small percentage, through resort to the method of Ducleaux, as modified by Byer,³ this conclusion arising from parallelism of graphs, charted according to the above method.

Insoluble Fatty Acids.—The caked acids, obtained as above, were

¹ *J. Soc. Chem. Ind.*, 6, 494 (1886).

² Lewkowitsch, 9.

³ *J. Biol. Chem.*, 28, 445 (1917).

repeated, recaked, and found to constitute 89.8% of the oil. This combined mass of saturated and unsaturated acids of higher carbon content gave the following constants: saponification value, 195.9; iodine value, 96.6; mean molecular weight, 286.

Saturated Acids.—44.4 g. of the oil was subjected to the lead salt method of Gussarow-Varrentrapp, with Tortelli's modifications,¹ to separate unsaturated from saturated acids. By this process, we found that, of the total insoluble acids 85.3% were unsaturated and 14.7% saturated. The 2 types were examined as to their chemical constants, with following results: solid acids, iodine value, 24.4, neutralization value, 187.3; unsaturated acids, iodine value, 123.8; neutralization value, 314.

An attempt was made to separate the individual solid acids by a fractional precipitation through use of barium and magnesium salts, and through the use of lead acetate in alcoholic solution, but, after repeated trials, these methods were abandoned as affording little prospect of any definite approach to a quantitative separation. We finally accomplished this separation by first dissolving the solid acids in absolute alcohol, using least possible volume, and successively lowering our alcohol concentration, by the admixture of water, to conditions which induced the next sign of precipitation. By this method 3 fairly distinct fractions were obtained, all crystallized as fine needles, whose melting and solidifying points were found to be as follows

Fraction.	% Alcohol in solvent	Melting point (<i>corr.</i>)	Solidifying point (<i>corr.</i>)
A	70.0	64-73	64-65
B	60.0	57-64	55-57
C	50.0	52-57	51-51.5

Fractions A, B and C were refractionated by the same process as mentioned above, with the following results

Sub-fraction.	% Alcohol by vol	Melting point (<i>corr.</i>)	Neutralization equiv.
A ₁	70.0	72.2	366
A ₂	50.0	Fraction too small for accurate determination	
B ₁	70.0	62.8	254
B ₂	65.0	62.5	..
B ₃	60.0	62.4	..
B ₄	50.0	62.6	...
C ₁	50.0	56.7	273
C ₂	40.0	Fraction too small for detn.	

Fractions B₁, B₂, B₃, B₄ were combined, recrystallized from 70.0% alcohol, and a melting point of 62.7°, and the above neutralization value of 254, determined from this product. From above data and from usual solubility tests, the crystals were identified as those of palmitic acid, which constitutes approximately 80% of the entire amount of solid acids.

¹ *J. Ind. Eng. Chem.*, 9, 542 (1917).

Fraction A₁ was converted into its lead salt, which had a melting point of 113°, uncorrected, and was insoluble in ether. These facts, together with the neutralization value of the acid, raised a presumption that it might be carnaubic acid. The acid was analyzed, with the following results:

Calc. for C₂₄H₄₄O₂: C, 78.26, H, 13.04. Found: C, 78.37; H, 13.19.

The lead salt of fraction C₁ was made and its melting point fixed at 105.5°. This, with the melting point of the acid itself, 56.7°, pointed to daturic acid, and this conclusion was confirmed by combustion.

Calc. for C₁₇H₃₄O₂: C, 75.56, H, 12.59. Found: C, 75.42; H, 12.70.

As no other crops of crystals, appreciable in amount, were observed, our solid acids were presumed to be composed of a comparatively large amount of palmitic acid, with less quantities of carnaubic and daturic acids.

Unsaturated Acids.—These acids were prepared by the lead precipitation method, whereby we obtained a voluminous nearly white oil-mass, whose iodine number was 124, and mean molecular weight 314.

In order to determine the individual acids of this mass, we had recourse at first to the method of bromination. But, even after our samples had stood for 24 hours in contact with the brominating mixture and in the cold, we found but slight traces of a solid product. We inferred, by reference to the work of Jacobson and Holmes,¹ who assert that this method secures satisfactory results only in case of linolenic acid, when applied to such mixtures as we were investigating, that we have here no considerable amount of linolenic acid.

We then resorted to the well-known method of Hazura.² 24 g. of the unsaturated acids was saponified and the resulting soaps were oxidized by the above method, when a heavy precipitate of the hydroxy acids settled out on standing in the cold overnight. This mass, on filtering it out and allowing it to dry spontaneously to constant weight, gave us a dry product of 9.3 g. The filtrate, which might contain hexahydroxystearic acid as an oxidation product of linolenic or isolinolenic acid, was evaporated to a small volume and acidified with sulfuric acid. The resulting brown flocculent mass was extracted with ether and the only product which we could obtain was that embodied in the extract, which gave us a very small quantity of crystals in the form of flat, rhombic plates, obtruncated. We lacked material to obtain its major characteristics, but concluded from our meager data, that we had a small amount of the iso type of linolenic acid in our oil.

The main precipitate of hydroxy acids, washed with ether, was exhausted with 4000 cc. of ether, and from the ethereal solution we obtained,

¹ *Am. Chem. J.*, 38, 482 (1907).

² *Monatsh.*, 8, 260 (1887).

by evaporation to 150 cc. and cooling, 4.8 g. of crystals which were rhombic in shape. These crystals were found to have a melting point of 139.4° (corr.), concordant through 6 trials, and a neutralization equivalent of 318. Dihydroxystearic acid was thus identified. By calculation to oleic acid, it was evident that of our total oxidized unsaturated acids, 51.6% consisted of oleic acid. We found that this hydroxylated acid was insoluble in cold water and cold alcohol, but readily soluble in hot alcohol, which was used for all recrystallizations.

The solid remaining after extraction of the above fraction with ether was boiled out repeatedly with much hot water, each time filtered while hot, and allowed to deposit crystals on slow cooling. In this manner we obtained a final separation of the whole mass of crystals, into 7 fractions which were filtered, dried at 100° to constant weight, and subjected to test as to melting point and neutralization value, as follows:

Fractions	I.	II	III	IV	V	VI.	VII
Melting pt. (Corr.)	158.3°	158.0°	159.3°	173.7°	173.9°	173.7°	173.6
Neutral. value	351	355	353	347	348	346	344

Fractions I, II, III were combined, as were Fractions IV, V, VI, VII and each recrystallized from hot water, their constants being determined as before and as follows:

Fraction	I-II-III	IV-V VI VII
Melting pt. (Corr.)	159.9°	173.4°
Neutral value	354	349

The first combined fractions (I, II, III), when recrystallized, separate in leaflets which were long, oppositely truncated parallelograms. The second combined series of fractions gave, on recrystallization, silky needles when deposited from the hot water medium. The fraction melting at 173.4° was thus easily identified as tetraoxystearic acid, from original linolic acid, and its amount, 1.9 g., indicated that, of the unsaturated acid which we succeeded in oxidizing, 20.4% was in the form of linolic acid.

The second combined fraction, with neutralization value so close to that of the tetrahydroxy acid above mentioned, but markedly differing in melting point, we considered to be an isomeric form of the tetra acid and its amount, 2.2 g., indicated that 23.7% of the original oxidized acids was an iso-linolic acid.

We, therefore, conclude that our unsaturated acids are composed largely of oleic, linolic and an iso form of linolic acid.

Unknown Solid.—We examined the white crystalline solid, mentioned elsewhere in this paper as being allied in several particulars to a phytosterol but radically differing from this class of substances in its extreme high melting point, which was found to be unvarying at 279° , corrected. The substance contains only carbon, hydrogen and oxygen.

The fuchsin test for aldehydes gave negative results, pointing neither to the presence of aldehyde grouping nor to any polymerized form thereof.

The product was carefully tested for the presence of acid, carbohydrate, phenol, ester, anhydride, lactone and ketone grouping. In none of these tests did we derive any positive results, excepting the application of the hydroxylamine method for ketones, where we obtained a slight test for the ketone structure, unsatisfactory in its intensity and amount of precipitate, but nevertheless positive.

We applied the usual acetylation test for the presence of alcoholic radicals, and obtained positive and satisfactory proof that the substance under examination is an alcohol.

The product was analyzed with the following results:

Analyses	I.	II.	III.	IV.	Average.
Carbon-%	80.52	80.71	80.86	81.10	80.8
Hydrogen-%	10.16	10.39	10.00	9.90	10.1

By calculation from above data, we derive an empirical formula of $C_{12}H_{14}O$.

Using chloroform as solvent, we obtained molecular weight data as follows, employing the Liebig method:

Analysis	I.	II.	III.	IV.	Average.
Mol wt	372	354	350	349	356

The product was also examined by the Menzies method of vapor density, to determine its molecular weight, as follows:

Analysis	I.	II.	III.	Average.
Mol wt	378	362	367	369

In the latter manipulations, we used carbon disulfide as solvent, finding that other usual solvents gave us unconcordant results, evidently due to association.

We would, therefore, assign to this product a tentative molecular formula of $C_{24}H_{28}O_2$.

The product is soluble in hot ether, hot alcohol, chloroform, carbon disulfide, carbon tetrachloride, xylene, benzene, and slowly soluble in pyridine, acetic anhydride, and ethyl acetate. It is insoluble in water or cold alcohol. With a mixture of one cc. of acetic anhydride and 2 drops of conc. sulfuric acid, it assumes a purple coloration, which rapidly deepens to wine-red.

Some light was thrown upon its structure by the fact that when an amount of the purified product corresponding to its apparent molecular weight as determined above, was treated with theoretical amounts of the proper reagents, a substance was obtained which we identified as fluorescein. This would indicate that two side chains, in *ortho* position to a nuclear ring, are to be found in the structure.

So far as we have been able to gain access to the literature, we find no product which corresponds to this substance to have been noted. We, therefore, venture to claim that this oil carries an alcohol-ketone, in several respects allied to the phytosterols, in other regards differing markedly from such types, and have named this solid product, pending its further examination, "Prosol."

Summary.

The oil of proso millet is a semi-drying oil, capable of classification in this regard, with oils of sesame, rape and peanut

It is essentially composed of glycerides of the following fatty acids palmitic, oleic, linolic, iso linolic, and in smaller percentages, carnaubic and daturic

The solid acids from such an oil can best be separated through their fractional precipitation from a series of varying concentrations of alcohol in water, with fairly constant differences between successive concentrations.

The bromination method seems inadequate for the satisfactory separation of individual members of the un-saturated fatty acids from similar oils

A ketone alcohol, insoluble in water, soluble in certain organic solvents, and possessing certain properties similar to those of a phytosterol, is a by-product in the preparation of this oil, as the authors prepared it for analysis. So far as they have been able to ascertain, this product has not been discussed in the literature pertaining to plant products.

BROOKINGS S D

NEW BOOKS.

Verdampfen, Kondensieren und Kühlen. By F. HAUSBRAND 6th Edition 1918
53 figure, 5113 tables 340 + xix pp Julius Springer, Berlin 16 Mk.

This edition contains much new material, formulas, tables, and examples, from investigations prior to 1918 which should be helpful in the design, construction and operation of apparatus for evaporating, condensing or cooling. It contains 37 more tables and 140 more pages than the second English edition of 1916. Much of the book has been rewritten with new material in almost every chapter. A number of tables have been changed to conform with later investigations. Noteworthy are the additions on heat transfer in liquid and vapor cocurrent and counter current systems; in heat interchangers, and preheaters, in evaporators using hot liquids; in still steam through cold tubes; and in systems using air, gases, and superheated water vapor. The section on multiple effect evaporators has been entirely recast to show more clearly the function of each unit in the multiple system. Most of the new data have been taken from German engineering publications.

T. R. CHURMAN.

Lehrbuch der Physikalischen Chemie. By DR. KARL JELLINKE. In 4 books: Book I only now published. Ferdinand Enke, Stuttgart.

The author has undertaken what promises to be by far the most comprehensive treatise of Physical Chemistry that has been attempted. The only one approaching it in scope is that by W. Ostwald "*Lehrbuch der allgemeinen Chemie*," the first part of the second edition of which appeared about 1891. The text-books of physical chemistry by W. Nernst, J. H. van't Hoff as well as those by English and American authors are necessarily brief in their treatment of this field and in some instances omit entirely certain important phases of the subject. It is true, as pointed out by the author, that in most of these books chemistry has been emphasized very much more than physics. In view of the remarkable advances which have been made in both physics and chemistry during the last two or three decades, the author has felt that there is a place for an extensive treatise on physical chemistry in which this vast amount of information is properly systematized and in which the two sciences, physics and chemistry, are properly correlated.

For purposes of presentation, the subject has been divided as follows: Book I, Vols. I and II, "*Die Lehre von den Aggregatzuständen (reine Stoffe und verdünnte Lösungen der Nichtelectrolyte)*;" Book II, Vol. III, "*Die Lehre von Aufbau der Materie (Weltäther, Electronen, Ionen, Atome und Molecule)*;" Book III, Vol. IV, "*Die Lehre von den Umwandlungen der Materie (chemische Statik und Kinetik)*;" Book IV, Vol. IV, "*Die Lehre von den Umwandlungen der Energie (Mechanochemie, Thermochemie, Magnetochemie, Elektrochemie, Photochemie)*."

Book I, Vol. I (part 1), "*Die Lehre von den Aggregatzuständen*," xxvi + 733 pp., 253 figures, 81 tables. 1914. Price, 27 Mk.

The author has considered 5 states of aggregation, the gaseous, the transitional (gas to liquid), the liquid, the fluid and the solid. The first 3 are fully treated in Vol. I. The first portion of this volume serves as a general introduction to the subject of physical chemistry, discussing atomic theory, perfect gas laws, molecular theory, law of conservation of energy, principle of the increase in entropy and Nernst's heat theorem. It contains an exceptionally complete and well systematized bibliography not only of the important books and journals of various branches of chemistry but of physics and, to a lesser extent, of mathematics as well. A detailed table of contents and an author and subject index are included in both volumes.

Book I, Vol. II, (part 2). "*Die Lehre von den Aggregatzuständen*," xii + 939 pp., 401 figures, 149 tables. 1915. Price, 35 Mk.

This volume contains a thorough treatment of the fluid and solid states of aggregation as well as of gaseous and liquid solutions. A discussion

of colloidal solutions is not included as was originally planned, but is to form the subject of a later volume. The electrical, magnetic and optical properties of pure substances have not been considered in Book I, but will be treated in Book II.

The subject matter of these two volumes is well arranged, clearly written and in general very complete. As an illustration of the character of the material presented, the subjects treated under kinetic theory may be mentioned. They are Maxwell's law of distribution of velocities, rigorous derivation of the gas law from kinetic theory, concept of the degrees of freedom, rotation of gas molecules, vibration of atoms in gas molecules, principle of the equipartition of energy and the various degrees of freedom of a molecule in stable condition, theory of specific heat of gases from the standpoint of the classical kinetic theory and of the quantum theory. In addition to the theoretical treatment the most important experimental methods are given in considerable detail. The numerous drawings and the experimental data in tabular and graphic form make this feature of the work very valuable to both student and investigator.

The author has attempted to present the material from the pedagogical as well as from the experimental standpoint. A knowledge of the fundamentals of chemistry, physics and mathematics (calculus) is presupposed. Where higher mathematics is employed the development is more fully given. If the remaining three books are up to the standard of their first book, the work will indeed be a real contribution to this field of science.

JOSEPH M. BRAHAM

Notions Fondamentales de Chimie Organique (5th edition) by CHARLES MOUREL, Membre de l'Institut et de l'Académie de Médecine, Professeur au Collège de France, Gauthier-Villars et Cie, Paris, 1910. viii + 315 pp. 11.5 X 23 cm. Price, 16 Fr.

This work is meant to give a thorough grounding in the fundamentals of organic chemistry, and is written for university students. It will be found less detailed than the usual American elementary text, especially in regard to industrial applications and theories of the mechanism of reactions. It seems to presuppose some familiarity with the laboratory behavior of organic substances.

The book is divided into two parts, each of which presents features of interest. The first chapter, a third of the whole in length, treats briefly those aspects of general and physical chemistry of most importance to organic chemists. A clear and readable but quite elementary exposition of the atomic and molecular theories, such as is usually given in a first year course in chemistry, is followed by an all too brief and dogmatic discussion of valence and structural formulas. A large number of methods for the determination of molecular and atomic weights are listed, but

without experimental detail. Substitution leads to homology, the classification of organic substances, and nomenclature.

In the section on stereochemistry which follows (33 pages) the author has allowed a desire for thoroughness to win him from that allegiance to symmetry and balance which distinguishes the rest of the book. The later use of the subject in the special part is hardly sufficient to justify so detailed an account. Up to and including the discussion of the relation of physical properties to chemical constitution, the reviewer is unconvinced of the value of the method of treatment used. If the book is meant for beginners, too much acquaintance with phenomena is implied, while students with sufficiently rich backgrounds to get full benefit from the introduction certainly deserve a more comprehensive and interpretative treatment of the subject matter.

The most interesting part of the introductory chapter is that which deals with chemical kinetics, "active" molecules, and the general contrasts between organic and inorganic reactions. Here a dash of calculus is somewhat apologetically introduced, and the laws of reaction velocity and equilibrium are clearly and usefully stated, without thermodynamic derivations. Chemical affinity and chemical potential, together with the influence of various forms of energy on reactivity, are treated in a simple and wholly non-mathematical way. Catalysis receives some attention. Considering its unavoidable superficiality and the infrequency of its use in the special part the whole general introduction seems of questionable value.

Chapter II begins the systematic presentation of the chemistry of the hydrocarbons and their derivatives. The method of arrangement, the selection of the illustrations, and the *enchainment* of the thought are all well suited to the purpose of the book—the development of that ability to "feel" what reactions will "go" and how they will go, which is of first importance in the training of a skilled structural chemist. Acyclic hydrocarbons of all series, with their halogen and nitro derivatives, are followed by the cyclanes and the aromatic series. Here in addition the sulfonic derivatives are introduced, and the chapter ends with 2 pages on the terpenes. Alcohols, ethers and phenols are next discussed at length, followed by aldehydes, ketones, and quinones. The acids, particularly aldehyde- and ketonic acids, lead naturally to the sugars, their stereochemistry and synthesis, and the chapter concludes with other carbohydrates and glycosides.

In Chapter IV amines and diazo compounds, nitriles, isonitriles and amides are followed by the ureids and the purine group. "Inorganic" derivatives receive scant attention. A dozen pages on heterocyclic compounds conclude the systematic part.

Dyestuffs are reserved for the final chapter—a 40-page monograph,

NEW BOOKS.

which is a model of ordered arrangement and judicious exclusion. This chapter does not form a necessary part of the whole and might have been omitted without impairing the development of the thought; or, of course, any number of similar chapters (poisons, perfumes, etc.), might be added in the same way.

The table of contents is adequate and the index quite unusually detailed and complete for a French text. There are no cuts. The typography is excellent on the whole, though occasionally one misses the third bond of a triple linkage, and Mr. Shields might well object (p. 24) to the teutonization of his name to Schields. The spelling both of "*evacuation*" (p. 79) and of its French derivative may possibly be charged to the printer. Very little is said about the probable mechanism of organic reactions, and such important subjects as the behavior of nitro-compounds and tautomerism do not seem to receive adequate treatment. When the mechanism of a reaction is discussed, the presentation is unfortunately too often dogmatic and unsupported by evidence. The absence of illustrations of industrial applications combined with the latter characteristic puts a rather severe strain upon the attention and risks making the close-knit and very condensed account seem monotonous.

In particular cases, this extreme condensation leads to positive inaccuracies, as when (pp. 171-172) in the 2-page discussion of conjugated systems of ethylene linkages and the theory of partial valences, one is left with the impression that 1,4 addition is the invariable rule in such systems, or when on p. 190, the author says of *trimethylene* (hexamethylene, and the cyclanes in general), "they have not the chemical characteristics of unsaturated hydrocarbons—thus with chlorine and bromine they give substitution— and never addition-products." Binary mixtures (p. 106) do not "always melt much lower" than their components. The author uses "quadri-" and "tetra-valence" with a hearty indifference and does not scruple to describe lack of reactivity as "stability." On pp. 8-9 some of the statements regarding the molecular condition of various forms of matter might be made with more reserve.

Certain peculiarities of emphasis are hard to understand, but, on the whole, the selection has been excellently made, and the book is a fine example of French mastery of form and *mesure*. NORRIS F. HALL

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American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

**ELECTRO ENDOSMOSIS AND THE PREPARATION OF SOLID
ALKALI AMALGAMS.**

BY SUMNER B. FRANK AND JAMES R. WITHROW.

Received December 1, 1919.

It was found when using the Shepherd method of making solid amalgams that increasing the current applied to a given cathode area and allowing adequate time, accelerates otherwise sluggish electro endosmotic effect with the porous cups and electrolytes used. The observations of G. McP. Smith and Bennett on the electro preparation of solid alkali amalgams were substantially confirmed in the cases tried, namely with potassium, barium, strontium and calcium. The use of low temperatures and non-aqueous electrolytes made no improvement over earlier efforts to produce solid calcium amalgam electrolytically.

The Shepherd Method of Making Solid Amalgams.—Shepherd¹ suggested an improved method of making solid amalgam by electrolysis. He supported a porous cup containing the mercury as cathode, so that the cup was submerged but slightly in the anolyte and used less than 8 volts. It had been noticed in previous work with this method² that electro endosmosis developed; in fact this was a difficulty in that method which

¹ *J. Phys. Chem.*, 7, 29 (1903).

² G. McP. Smith and Withrow, *THIS JOURNAL*, 29, 321 (1907).

had to be overcome. One of the present writers has been in the habit of utilizing this difficulty as a convenient lecture demonstration of the phenomenon of electro endosmosis, to furnish a ground work for the discussion of permeable diaphragm cells for chlorine manufacture.

Electro Endosmosis with the Shepherd Cell.—Complicated apparatus has been used customarily in the study of electro endosmosis.¹ Some of the forms of apparatus employed by these workers could be used for lecture demonstration, but they lack the directness of appeal of bare, porous-cup demonstration of the effect, such as a modification of Shepherd's porous-cup method for the preparation of solid amalgams can be made to give. The latter apparatus is simple, and expensive platinum cathodes are eliminated. Striking manipulation is made possible by beginning the demonstration with the bottom of the porous cup containing the mercury cathode submerged but a few millimeters below the level of the anolyte. Upon electrolysis for less than an hour, starting with the cathode cup entirely free of electrolyte, the endosmosed liquid will rise within the cell over the mercury several centimeters above the outside level of electrolyte and may be poured out of the porous cup as a visible, measurable demonstration of the electro endosmotic effect.

After considerable use of the method, unexpected failure to get any effect at all, in some trials, rendered necessary a laboratory study of the proper conditions for the Shepherd experiment as an illustration of the endosmosis phenomenon. The statements in the literature as to the essentials governing the phenomenon are vague or non-concordant. Stewart² says the current must be "sufficiently strong." Wiedemann,³ states that the phenomenon is dependent on current strength and independent of the area or thickness of the diaphragm. Byers and Walter⁴ state "the flow of liquid through the septum is proportional to the intensity of the current." Briggs, Pierson and Bennett⁵ state "the volume of liquid transported in unit time is directly proportional to the external potential applied."

¹ Morse and Olsen, *THIS JOURNAL*, 23, 437 (1900). Reed, *Trans. Am. Electrochem. Soc.*, 2, 247 (1902), Frazer and Holmes, *ibid.*, 40, 320 (1908), Bancroft, *Trans. Am. Electrochem. Soc.*, 21, 233 (1912); Byers and Walter, *THIS JOURNAL*, 36, 2284 (1914); Taylor, "The Chemistry of Colloids," p. 66-74, New York, Longmans, Green and Co., 1915; Briggs, Pierson and Bennett, *Trans. Am. Electrochem. Soc.*, 31, 257 (1917).

² "Recent Advances in Physical and Inorganic Chemistry," p. 94. Longmans, Green and Co., New York.

³ "Text Book of Electro Chemistry," p. 157, LeBlanc, trans. Whitney and Brown, Macmillan Co., New York, 1907.

⁴ *Ibid.*

Experimental.

The work in the two previous papers¹ on the porous-cup method of making solid amalgams was repeated for the purpose of observing the relationship of the electro endosmotic effect to other conditions. The results given in the following table are typical.

TABLE I.

Expt	Electrolyte	Mercury used G.	Current		Cathode amps	Maximum temperature		Time Min	Endosmosis mm.
			Ampères	Volts		Cup °C	Analyte		
1	KCl	60	1.8-3.0	12.5-13.5	41-60	95.5	67	29	0
2	50 cc. —K ₂ SO ₄	69	1.0-1.7	19-22	23-39	95	63	24	5
3	50 cc. —K ₂ SO ₄	64	0.2	8	5	30	28	66	6
4	150 cc. —K ₂ SO ₄	507	1.6-2.1	18-21	10-13	75	58	62	38
5	—K ₂ SO ₄	196	0.1-0.35	10	1.9-2.2	32	29	70	5
6	—K ₂ SO ₄	507	0.6-0.2	10	3.8-1.3	25	23	80	5
7	50 cc. —KCl	250	2.4-3.1	6		45		56	..
8	50 cc. —KCl	250	3.0	5.5-6		52		80	..
9	50 cc. —KCl	250	3.0	6		55		40	..
10	50 cc. —SrCl ₂	260	2.6-2.9	7.5-6.5		45		102	..
11	35 cc. —(CH ₃ C ₂ H ₅) ₂ Ca	150	1.3-2.5	10		70		68	..

Saturated solutions were used in beginning all experiments. The porous cups holding the mercury (cathode) were immersed 0.5 to 1.0 cm. in the electrolyte. Those used in Expts. 1 to 3 were 21 mm. and those in 4 to 6 were 40 mm. in diameter. Run 1 yielded a solid crystalline amalgam and yet no endosmosis took place. The cup had been soaked in water for 24 hours previous to the experiment. Expt. 2 was suddenly terminated by the deposition of a crust of salt on the outside of the cup. The cup had been soaked an hour before starting. The amalgam was solid when poured into water at 22°. In Expt. 3 a low voltage was used to find the influence of such voltage on osmosis using nearly triple the time of Expt. 2. Solid amalgam was not produced. The cup had been soaked 45 minutes previous to the experiment. Expt. 4 duplicated the conditions and results of Smith and Withrow,² using a common but different make of porous cup of 4 x 8 cm. There accumulated 38 mm. of solution on top of the amalgam and it was still rising when the current was stopped, though solid amalgam was not reached. In Expts. 5 and 6 with lowered voltage using the same cup, no electro osmosed solution appeared until after 28 to 30 minutes. This showed the depressing effect on electro endosmosis of lowered voltage and the concomitantly lessened current flow. It appears from these results that the electro endosmotic effect is somewhat modified by the character of the porous cell used, but any failure to appear or any retarding action can be overcome in all the

¹ Shepherd, *loc. cit.*; and Smith and Withrow, *loc. cit.*

² *Ibid.*

types of cup at our disposal by raising the voltage (increasing the current density). The exact figure will vary with the individual cup, but we found steady endosmosis, using 20 to 25 volts in place of the 6 to 8 volts of Shepherd on amalgams. This conclusion is borne out by the experience recorded by Smith and Withrow,¹ who used as high as 22 volts in one case, but did not note its influence. A study of the relation between porosity and this endosmotic effect, as well as the relation of other factors, would be of further interest, but was not necessary to accomplish our object. Potassium sulfate appears to be more satisfactory than the chloride. The Shepherd mercury cathode cups appear to have advantages for the study of this phenomenon of whose bearing upon the design and operation of commercial alkali-chlorine diaphragm cells there is too little appreciation. The matter merits further study.

Lecture Demonstration of Electro Endosmosis with the Shepherd Cell.

For the Shepherd device as a lecture demonstration of electro endosmosis, one should use a good grade of porous cup about 40 X 80 mm. It should be held by a clamp so that it visibly extends one cm. or less below the level of the anolyte, preferably saturated potassium sulfate solution contained in a beaker. The whole should be supported so that heat may be applied if necessary. A layer of mercury 5 mm. deep as cathode within the porous cup is electrically connected by a platinum point protruding from the usual glass seal connection. To facilitate prompt action the cup may be soaked in a dilute solution of the electrolyte overnight prior to the demonstration. Any form of platinum anode may be used in the beaker containing the anolyte. Twenty to twenty-five volts will suffice to enforce electro endosmosis with the ordinary porous cup.

Solid Alkali-Amalgams.—In the course of the work on electro endosmosis there was opportunity for parallel runs for the electro production of solid alkali-amalgams by other methods. Examples of these are given (Expts. 7 to 11) in the above table. In all of these cases the procedure of Smith and Bennett² was followed.

Potassium Amalgam.—When poured into water, Expt. 7 gave a thick but not solid amalgam due to furnishing a larger area for decomposition than did Smith and Bennett. Using the same size beaker as used by them, after 10 minutes in Expt. 8, crystals of amalgam began to form on top of the mercury³ and rapid evolution of hydrogen took place when the crystals were not constantly stirred into the mercury. Upon pouring into cold water the amalgams did not form a solid cake, but masses of fine crystals could be fished out with the fingers. The product of Expt.

¹ *Loc. cit.*

² *THIS JOURNAL*, 31, 799 (1909).

³ *J. Phys. Chem.*, 20, 530 (1916).

9, where crystals began to form in about 15 minutes, did solidify when poured into a beaker of water surrounded by ice. The amalgam remained solid at 5°.

Strontium Amalgam.—In Expt. 10 there was a 24-minute interruption in the middle, due to cessation of current. The resulting amalgam was too thick to pour and when it was dumped into cold water it appeared solid or in a very thick semi-solid state. The cessation of the current was due to the fouling of the platinum wire by an accumulation which shut off the current.

Calcium Amalgam.—In Expt. 11 solid calcium acetate was added from time to time. After 2 or 3 minutes the solution became milky and turbid, and in 10 minutes it became black and a thick, gray mixture of calcium hydroxide and mercury was obtained as in our previous work. Repetition in a freezing mixture gave no improvement. Experiments with non-aqueous solutions such as calcium bromide in absolute ethyl alcohol, and calcium chloride in methyl alcohol,¹ all gave the same results as aqueous solutions. Patton had deposited metallic calcium on platinum electrodes from the last electrolyte but stated that the hydroxide was deposited from ethyl and amyl alcohols. The preparation of solid calcium amalgam seems to depend upon the prevention of the formation of the hydroxide which is greatly accentuated in the case of calcium, is present in the case of strontium, but practically lacking in the case of barium. It is possible that electrolysis in solutions at just about their freezing points, might give satisfaction, or below the freezing point of water in the case of organic solvents. The observations of Reed² and of Haber,³ on the projection of metallic lead into the solution when aqueous sodium hydroxide is electrolyzed with lead electrodes would appear to have a suggestive bearing on the formation of the black mixture of metallic mercury and calcium hydroxide. The calcium amalgam attacks the electrolyte so strongly that it holds the mercury in finely divided state in the calcium hydroxide product.

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¹ H. E. Patton, *Jahrb. Elektrochem.*, 13, 429 (1903).

² *J. Frank. Inst.*, April, 1895

³ *Trans. Am. Electrochem. Soc.*, 2, 189 (1902).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

FURTHER STUDIES ON A LEAD STANDARD CELL.

BY M. G. MELLON AND W. E. HENDERSON.

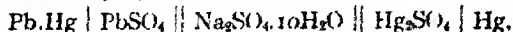
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Part I. Introduction.

A. General.—It is now well recognized that there is neither a large number nor a wide variety of types of arrangements suitable for the chemical combination known as a standard cell, the important, ultimate standard employed in the establishment of the unit for the intensity factor of electrical energy (electromotive force)—the volt.

The requirements for such combinations have been pointed out at various times, and many efforts have been made to select the most satisfactory ones.¹ For their construction Hulett² and his co-workers conclude that, in addition to mercury, "zinc and cadmium are the only two metals which fulfil the (required) conditions,"—and, "it is improbable that the other metals will be found of service in standard cells."

In an earlier paper³ there were presented the results of certain work done in this laboratory upon a lead cell, consisting of the arrangement



in which Pb.Hg represents a saturated amalgam,⁴ and $\text{Na}_2\text{SO}_4.10\text{H}_2\text{O}$ represents a solution in equilibrium with an excess of sodium sulfate decahydrate. (Similar cells, using unsaturated amalgams, were also studied; but such cells, although sufficiently constant, are not easily reproducible since their electromotive force is a function of the concentration of the lead in the amalgam.) Because of its constancy, ready reproducibility,

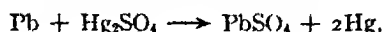
¹ A complete bibliography is too extensive to mention here, but the following will furnish the important references: Jaeger, "Die Normalelemente," (1902); Abegg-Auerbach-Luther, "Measurement of Electromotive Forces of Galvanic Cells with Aqueous Electrolytes" (Bibliography to 1910); "Bulletins of the Bureau of Standards," Reports of the Physikalisch-Technische Reichsanstalt, Reports in *Bull. Soc. Intern. Elect.; Chem. Abs.*—Decennial Index, p. 2550 (Work from 1907 to 1917); Certain references not included above, Carhart and Hulett, *Trans. Am. Electrochem. Soc.* 5, 59 (1904); Carhart and Hulett, *ibid.*, 6, 109, 118, (1904); Wolff, *ibid.*, 3, 49 (1904); Hulett, *ibid.*, 7, 733 (1905), 9, 239 (1906), Wilsmore, *Z. Electrochem.*, 10, 685 (1904); Steinwehr, *ibid.*, 12, 578 (1906), Reinders, *Z. physik. Chem.*, 43, 238 (1903); Barnes, *J. Phys. Chem.*, 4, 339 (1900); Barnes and Lucas, *ibid.*, 8, 196 (1904); Comm. Report, *Chem. News*, 90, 225 (1904).

² *Trans. Am. Electrochem. Soc.*, 14, 65 (1908); THIS JOURNAL, 38, 20 (1916).

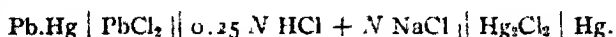
³ Henderson and Stegeman, THIS JOURNAL, 40, 84 (1918).

⁴ Gouy, (*J. physique*, 4, 320), gives the solubility of lead in mercury as 1.3%. As noted previously, Puschin has shown that amalgams containing between 1.8% and 66% exhibit the same electromotive force; and Fay and North state that amalgams containing between 2% and 55% are 2-phase systems, consisting of a granular phase of constant composition (Pb₂Hg), and a liquid phase which has also a definite composition, when equilibrium is reached.

and small temperature coefficient, this cell was suggested as a possible standard of electromotive force. The essential chemical reaction of the cell seems to be represented by the equation



in which the sodium sulfate does not function directly, but merely affects the solubility and the ionization of the sulfates of lead and mercury. This cell resembles the one studied by Babinski,¹ having the arrangement



B. Object of the Present Investigation.—In the earlier work preliminary experiments with cells containing potassium sulfate instead of sodium sulfate indicated that the former salt could not be used in such a combination. Since the above type of cell differs from the Weston and the Clark cells in that it contains one more solid phase and one more component, and since it may offer, therefore, a possibility of some secondary reaction, such as the formation of a double salt, the present work was undertaken, having as its object (1) the determination of the effect on the electromotive force of the cell arising from the substitution for the component mentioned above, of other components, such as would be supplied with the use of other well-defined, soluble sulfates; and (2) an inquiry concerning the possible cause for any difference between the electromotive forces of the cell containing sodium sulfate and those containing the other sulfates.

Cells were constructed, therefore, using not only sodium sulfate, but also, in its stead, the well-defined, soluble sulfates of potassium, lithium, magnesium, nickel, cobalt, zinc, manganese, cadmium, and copper. The following pages present an account of the experimental methods employed, the measurements made together with a discussion of them, and the results of work done because of certain observations made during the earlier part of the investigation.

Part II. Experimental.

A. Apparatus.—The apparatus used was essentially the same as that employed in the earlier work. The measurements were made by the compensation method, using a potentiometer reading to 0.00001 volt, in connection with a correspondingly sensitive galvanometer. A lead accumulator furnished the compensating current, and 2 certified Weston standard cells, recently checked, served as references. All measurements were made at $25.0^\circ \pm 0.01^\circ$, as indicated by a thermometer standardized by the Bureau of Standards.

¹ Dissertation, Leipzig, 1906.

B. Source and Purification of Materials.—The original materials used for the preparation or the purification of the final compounds or metals were the best obtainable. Conductivity water¹ was used throughout the work for the preparation of solutions, recrystallization of salts, etc. The mercury was purified by the methods of Hildebrand² and of Hulett.³ The mercurous sulfate was prepared by the method of Hulett.⁴ Two recrystallizations were made on the lead nitrate.⁵ Lead sulfate was prepared as before⁶ and preserved under dil. sulfuric acid.

The lead amalgams were prepared electrolytically, following somewhat the method of Goodwin.⁷ In a small crystallizing dish were placed 2 porcelain crucibles. In one was a weighed amount of mercury (30 to 50 g.) under the surface of which dipped a platinum wire sealed into a glass tube, the whole serving as a cathode. In the other a circular anode of platinum foil about 2.5 cm. in diameter was suspended horizontally half way from the bottom. The dish was nearly filled with a 10% solution of lead nitrate, covering the crucibles. A current of approximately 40 milliamperes from a large storage cell served for the electrolysis. Assuming that the deposition of lead follows Faraday's law, 2 coulometers were placed in the circuit, a water coulometer to indicate when the approximately desired deposition should have taken place, and a copper coulometer for the more exact determination.⁸

The soluble sulfates used were recrystallized twice, and only those forms that are stable at room temperature were obtained and preserved. These salts included the following, and the methods followed were substantially those given in the references: The sulfates of sodium,⁹ potassium,¹⁰

¹ Mosley and Meyers, *THIS JOURNAL*, 40, 1409 (1918).

² *Ibid.*, 31, 933 (1909).

³ *Phys. Rev.*, 33, 307 (1911).

⁴ *Ibid.*, 32, 257 (1911).

⁵ Baxter, *THIS JOURNAL*, 37, 1027 (1915); Richards and Lemberg, *ibid.*, 36, 1332 (1914).

⁶ Henderson and Stegeman, *loc. cit.*

⁷ *Z. phys. Chem.*, 13, 596 (1894).

⁸ The validity of this assumption is now the object of a further investigation. A relatively thick coating of lead peroxide always formed on the anode, and the solution became distinctly acid. Since amalgams containing between 2 and 60% of lead show the same potential, the present work is unaffected by this uncertainty, except for some question regarding the exact percentage of lead in the amalgams. All those used contained a solid phase.

⁹ Henderson and Stegeman, *THIS JOURNAL*, 40, 84 (1918); Richards and Yngve, *ibid.*, 40, 164 (1918).

¹⁰ Carveth, *J. Phys. Chem.*, 2, 300 (1898); Abegg, "Handbuch. Inorg. Chem.," 1, 377 (1908).

lithium,¹ nickel,² zinc,³ cadmium,⁴ magnesium,⁵ cobalt,⁶ manganese,⁷ and copper.⁸

C. Construction of Cells. (a) **Saturated Cells.**—In the case of all saturated cells, the paste was prepared and the cell constructed, in general, according to the method of Henderson and Stegeman. The following should be added: the excess solution of lead nitrate in the crucible over the amalgam was displaced by water and then by the solution of the sulfate being used for the cell. Some of the latter solution remained over the amalgam until its transfer to the cell in order to prevent oxidation.

(b) **Unsaturated Cells.**—No solid, soluble sulfate was used in the paste in the unsaturated cells, and the saturated solutions of sodium sulfate, etc., used above were replaced by solutions which had been saturated at 20°, this temperature being below that prevailing in the laboratory.

D. Experimental Data. (a) **Preparation of Amalgams.**—From the weight of copper deposited in the copper coulometer was calculated the equivalent weight of lead which should have been deposited in the mercury cathode. This weight, together with the weight of mercury taken, formed the basis for the calculation of the percentage of lead in the amalgams.

(b) **Determination of the Electromotive Force of Cells of the Saturated Type.**—In reporting the results of the measurements made it is not possible to include all of them, since 80 new cells measured over the period of time studied resulted in a large number of individual determinations. Table I shows a typical series of measurements for one of the salts, nickel sulfate. It is also representative of the results for all cells showing a constant electromotive force. The time required for the attainment of equilibrium, as indicated by the constancy of electromotive force, varied widely. The cells containing zinc sulfate, for example, were constant in 4 days after their preparation, while those containing potassium sulfate never became constant.

¹ Abegg, "Handbuch Inorg. Chem.," 1, 138 (1908).

² Roscoe and Schorlemmer, "Treatise on Chem.," 2, 1309 (1913).

³ Roscoe and Schorlemmer, "Treatise on Chem.," 2, 657 (1913); Jaeger, *Wied. Ann.*, 63, 354 (1897); Hulett, *Phys. Rev.*, 32, 266 (1911); Lamb and Lee, *THIS JOURNAL*, 35, 1666 (1913).

⁴ Hulett, *loc. cit.*

⁵ Roscoe and Schorlemmer, *ibid.*, 634 (1913); Harkins and Paine, *THIS JOURNAL*, 47, 1158 (1919); Lamb and Lee, *loc. cit.*

⁶ Roscoe and Schorlemmer, *ibid.*, 1285 (1913).

⁷ Roscoe and Schorlemmer, *ibid.*, 1150 (1913); Friend, "Inorg. Chem.," 8, 307 (1915); Linebarger, *Am. Chem. J.*, 15, 225 (1893); Cottrell, *J. Phys. Chem.*, 4, 637 (1900).

⁸ McIntosh, *ibid.*, 2, 189 (1898); Carveth, *loc. cit.*; Henderson, "Inorganic Preparations" (unpublished book).

TABLE I.—CELLS CONTAINING NICKEL SULFATE, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.

Made March 11, 1919.	Temp. 25°.		Amalgam, 3.30% lead.
Date.	E. m. f.		
1919.	No. 18	No. 19	No. 20.
March 12.....	0.96465	0.96467
March 13.....	0.96465	0.96465	0.96465
March 14.....	0.96470	0.96467	0.96470
March 21.....	0.96465	0.96465	0.96465
April 1.....	0.96466	0.96466	0.96466
April 16.....	0.96465	0.96466	0.96466
April 30.....	0.96465	0.96466	0.96466
May 3.....	0.96465	0.96466	0.96466
May 24.....	0.96465	0.96466	0.96466
May 30.....	0.96465	0.96466	0.96466

Table II contains a summary of the results obtained for the saturated cells. The value recorded for the observed electromotive force, for cells showing a constant electromotive force, is the value maintained during the period of observation; while for those not showing constancy, it is an average of the values observed after the cells were a week old. The electromotive force of cells containing cadmium sulfate showed a rather consistent increase over the period of observation; but those containing magnesium or lithium sulfates did not, and in the case of potassium sulfate, the values varied widely from day to day.¹

Since the original combination was suggested as a possible standard of electromotive force, it was particularly desirable to obtain some measurements on the cells prepared 2 years earlier. Unfortunately, owing to faulty sealing, only one cell was found to be in good condition, the others having evaporated to such an extent that the electromotive force exhibited was unreliable. The one cell was measured along with the new ones, and it is noteworthy that its value practically coincided with those of the new ones containing sodium sulfate. The results for the latter cells indicated a verification of the earlier results. This undoubtedly points to a marked constancy, but further data is desirable on the question of constancy for a long period of time.

Neither ammonium sulfate nor calcium sulfate was of value for cells. The former reacts with mercurous sulfate; and the latter, because of its small solubility, does not prevent the hydrolysis of the same salt of mercury.

(c) **Determination of the Electromotive Force of Cells of the Unsaturated Type.**—Jaeger² has shown that Clark cells containing more than one hydrate of zinc sulfate exhibit considerable variation from the

¹ There was marked evidence of hydrolysis of the mercurous sulfate in the cells containing potassium sulfate, as shown by the appearance of the yellowish, basic salt, after they had been constructed a day.

² *Loc. cit.*

TABLE II.—SATURATED CELLS.

No.	Soluble sulfate	% Pb in amalgam.	Period of observation.	Observed e. m. f. Volts.	Average variation. Volts.
1.....	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	2 yr. 4 mo.	0.96466	± 0.00002
Days					
2.....	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	3.15	90	0.96466	0.00002
3.....		3.08	14	0.96466	0.00002
4.....		3.08	90	0.96466	0.00002
5.....		3.08	14	0.96466	0.00002
6.....		3.23	7	0.96465	0.00002
7.....		3.23	20	0.96465	0.00002
8.....		3.23	7	0.96466	0.00002
9 ^a	K_2SO_4	3.02	90	1.0300	0.005
10.....		3.02	90	1.0270	0.008
11.....		3.02	90	1.0260	0.010
12 ^a	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	2.98	75	0.9620	0.0010
13.....		2.98	75	0.9615	0.0007
14.....		2.98	75	0.9620	0.0005
15 ^a	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2.84	60	0.9608	0.0008
16.....		2.84	60	0.9600	0.0007
17.....		2.84	60	0.9610	0.0010
18 ^a	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	3.30	80	0.96465	0.00001
19.....		3.30	80	0.96466	0.00001
20.....		3.30	80	0.96466	0.00001
21.....	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	3.16	21	0.9489	0.0003
22.....		3.16	21	0.9490	0.0003
23.....		3.16	21	0.9489	0.0003
24.....	$\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$	3.38	30	0.9520	0.0010
25.....		3.38	30	0.9540	0.0012
26.....		3.38	30	0.9535	0.0012
27.....	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	3.36	30	0.96480	0.00001
28.....		3.36	30	0.96479	0.00001
29.....		3.36	30	0.96480	0.00001
30.....	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	3.39	30	0.96478	0.00001
31.....		3.39	30	0.96478	0.00001
32.....		3.39	30	0.96479	0.00001

^a Duplicate sets showed similar results.

expected voltage, and that the metastability of the system may persist for some time. It seemed possible that a similar cause might account for the unsatisfactory results in the above cells containing the sulfates of potassium, lithium, magnesium, and cadmium. Therefore, in order to preclude the presence of any unsuspected, solid phases in these cells, unsaturated cells were constructed for most of the salts, similar to Weston unsaturated cells. The solutions were saturated at 20° by stirring the soluble sulfate and lead sulfate for 3 hours, and filtering off the excess salts. These solutions were unsaturated, then, at 25°. Table III presents the results of the measurements. In the column indicating the salt used, the formulas employed indicate that the salt was not present as a solid phase.

On account of the hydrolysis evident in the cells containing saturated solutions of potassium sulfate, no unsaturated cells were constructed using this salt.

TABLE III.—UNSATURATED CELLS.

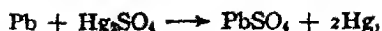
No.	Soluble sulfate.	% Pb in amalgam	Period of observation Days	Observed e m. f. Volts	Average variation. Volts.
1 ^a	Na ₂ SO ₄	3.58	55	0.96466	±0.0004
2.....				0.96466	0.0003
3.....				0.96466	0.0002
4.....	Li ₂ SO ₄	3.83	17	0.9620	0.0005
5.....				0.9610	0.0008
6.....				0.9600	0.0008
7.....	MgSO ₄	3.90	15	0.9615	0.0015
8.....				0.9600	0.0020
9.....				0.9622	0.0005
10 ^a	NiSO ₄	4.19	20	0.96430	0.00005
11.....			50	0.96430	0.00030
12.....			50	0.96433	0.00015
13 ^a	CdSO ₄	3.64	35	0.9520	0.003
14.....				0.9510	0.003
15.....				0.9530	0.003
16.....	ZnSO ₄	3.28	35	0.96478	0.00005
17.....				0.96477	0.00003
18.....				0.96476	0.00002
19.....	CoSO ₄	3.59	32	0.96478	0.0001
20.....				0.96478	0.0001
21.....				0.96476	0.0001
22.....	MnSO ₄	3.51	30	0.96478	0.00004
23.....				0.96478	0.00003
24.....				0.96478	0.00004

^a Duplicate sets showed similar results

(d) Evidence of the Formation of Double Salts. *Previous Work*.—The second effort to find some explanation of the erratic results obtained with certain cells was an attempt to determine whether any secondary reaction occurred in the cells, such as the formation of double or complex salts.

Several investigators¹ have studied the double salt potassium lead sulfate, the analyses showing the formula $K_2SO_4 \cdot PbSO_4$. Brönsted states that it is a finely crystalline powder, very similar to lead sulfate; and that it is always formed (for instance, on the addition of a solution of lead nitrate to one of potassium sulfate) instead of lead sulfate if the concentration of potassium sulfate is greater than 0.4%. He states, in his studies on chemical affinity, that the chemical reaction in cells containing sodium sulfate is represented by the direct electrode reaction:

¹ Becquerel, *Compt. rend.*, 63, 1 (1866); Ditte, *Ann. chim. phys.*, [5] 14, 190 (1878); Fox, *J. Chem. Soc.*, 95, 878 (1909); Barre, *Compt. rend.*, 149, 202 (1909); Brönsted, *Z. physik. Chem.*, 77, 315 (1911); Graham, *Z. anorg. Chem.*, 81, 257 (1915).



while that with the use of potassium sulfate is



The latter arrangement, because of the formation of the double salt, gives a considerably higher electromotive force, the difference between the 2 being a measure of the energy of reaction for the formation of the double salt.

He maintains further that the thermodynamical requirement that the electromotive force be independent of the concentration is fulfilled at 22°, but not at 60–100°, and that the lower temperature probably gives the correct values.

The values obtained by the authors for cells containing potassium sulfate¹ are somewhat lower than those of Brönsted. Furthermore, at no time was it possible to obtain with these cells such constant values as were reported by him.

Present Work.—The following methods were employed in a search for double salts in certain cells.

1. *Analytical.*—For the preparation of the suspected double salt, a 10% solution of lead nitrate was added slowly and with rapid stirring to a solution of 3 times its volume, nearly saturated with the sulfate being tested—potassium, lithium, magnesium, or cadmium. A second method was to reverse the process, adding the sulfates to the lead nitrate.

Analyses of the white products showed them to be only lead sulfate, except with the use of potassium sulfate, where the results corresponded to those found by Fox¹ for potassium lead sulfate.

2. *Microscopic.*—Examination under an ordinary microscope of the above salts, even after continued digestion in the mother liquor, revealed no characteristic difference between them and pure lead sulfate.

3. *Thermometric.*—Based on the statement of Brönsted¹ that the temperature of a saturated solution of potassium sulfate rises several degrees upon the addition of solid lead sulfate, owing to the heat of formation of potassium lead sulfate, the following method was adopted as a qualitative means of determining whether there was any thermometric indications of the formation of double salts:

Two large, insulated test-tubes, fitted with a stirrer to agitate the solution in each equally, were placed near together with a Beckmann thermometer in each. In one was placed about 25 cc. of a solution of potassium sulfate nearly saturated, and in the other an equal volume of water, all materials used being at room temperature. When the readings of temperature were changing equally, about 10 g. of solid lead sulfate was added to each tube and the readings continued. Similar experiments were made

¹ *Loc. cit.*

with mercurous sulfate, sulfuric acid of sp. gr. 1.15 replacing the water, since mercurous sulfate reacts with water.

On adding lead sulfate to the solution of potassium sulfate, the thermometer in the latter showed a marked rise, compared with the other instrument, which was still changing at the same rate as before. This was taken to be the result of an exothermic reaction between the lead and the potassium sulfates, and to indicate the formation of a double salt. No other combination tried, either with lead sulfate or with mercurous sulfate, showed any similar evidence of chemical reaction between the salts.

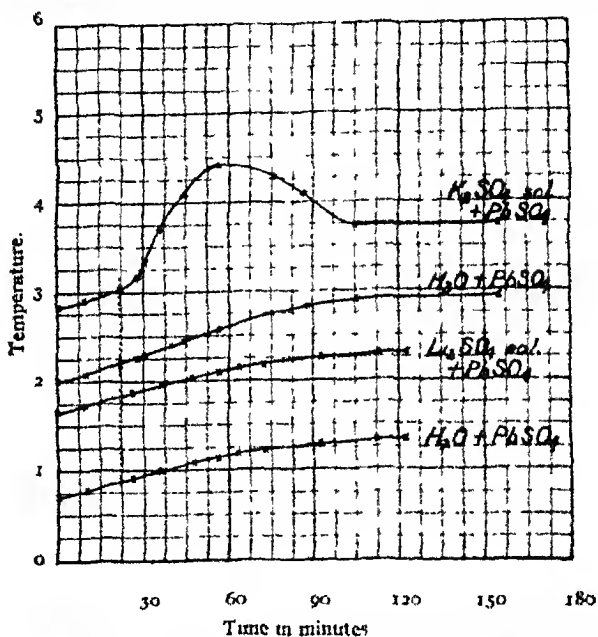


Fig. 1.—Changes in temperature of solutions of lithium sulfate and of potassium sulfate before and after the addition of solid lead sulfate to each. The dotted line indicates the time of adding the lead sulfate.

Fig. 1 is a graphical representation of the results for potassium and for lithium sulfates, in which time is plotted against change of temperature. Only constancy or inconstancy of the difference between the readings of the 2 thermometers, and not the actual values plotted, is of significance.

E. Discussion.—Among the fundamentally important points in the consideration of any combination as a possibility for a standard cell are its constancy, reproducibility, value of electromotive force, temperature coefficient, and possibility of showing hysteresis.

(a) **Constancy.**—Evidently for the period studied, these cells may be grouped into 3 classes: first, those showing marked constancy, and, apparently, meeting the requirements of a standard (a conclusion supported by the results for the one older cell)—these include the saturated cells containing the sulfates of sodium, nickel, cobalt, manganese, and zinc; second, those showing no constancy, including saturated cells containing the sulfates of potassium, lithium, magnesium, cadmium and copper, and unsaturated cells containing the sulfates of lithium, magnesium, and cadmium; third, those constant for a short time, including unsaturated cells containing the sulfates of sodium, nickel, cobalt, manganese, and zinc.

(b) **Reproducibility.**—In general, the reproducibility of the cells followed closely parallel with their constancy, that is, those showing a satisfactory constancy were readily reproducible, and *vice versa*. Satisfactory cells agreed with each other within 0.02 or 0.03 millivolt. An exception to this generalization occurred in the case of cells containing copper sulfate, which seemed to agree very well but showed some inconstancy. Also certain unsaturated cells, such as those containing sodium sulfate, agreed as long as they remained constant.

(c) **Value of Electromotive Force.**—The electromotive force of all constant cells was sufficiently large for the ordinary uses of standard cells, being nearly as large as that of Weston cells.

(d) **Temperature Coefficient and Hysteresis.**—The work of Henderson and Stegeman showed satisfactory temperature coefficients for the cells then studied. Further observations on this point and studies on the possibility of hysteresis are contemplated.

(e) **General.**—Brönsted's statement that the electromotive force is thermodynamically independent of the concentration of sodium sulfate seems to be somewhat confirmed, since the present saturated cells containing sodium sulfate practically agreed with the unsaturated ones (while constant). Also the electromotive force of the other constant cells, containing other salts, varied by only a small difference from the values for the cells containing sodium sulfate. For example, the 3 sulfates, cobalt, zinc and manganese, gave cells with a slightly higher electromotive force than the sulfates of sodium and of nickel, the latter 2 salts are less soluble, and hence, furnish a smaller concentration of dissolved salt.

It should be noted that the exact conditions of concentration and ionization prevailing in the systems studied are not simple. Using sodium sulfate, for instance, we have in the arm of the cell containing the amalgam the ions formed from the dissolved portion of the slightly soluble lead sulfate in the presence of the ions formed from the dissolved portion of the very soluble sodium sulfate decahydrate. On the one hand, because of the contribution of the common ion, SO_4^{--} , from the large excess of sodium

sulfate, one might expect some effect of mass action, resulting in a slight decrease in the solubility of the lead sulfate, and, therefore, in a slight change from the ionization relationships obtaining for lead sulfate in water alone. Also it is probable that, with the use of a salt having a solubility differing considerably from that of sodium sulfate, we might expect some difference in the magnitude of the effect on the ionization of the lead from lead sulfate, and, hence, a slight variation in the resulting electromotive force. The solubilities of sodium and of nickel sulfates are about the same at 25° and the electromotive forces of the 2 cells practically agree. Also the sulfates of manganese, cobalt, and zinc have a considerably higher solubility, and cells containing these salts gave a higher electromotive force; but from this standpoint the manganese sulfate should have given the highest. On the other hand, it must be borne in mind that some sparingly soluble salts are more soluble in salt solutions than in water alone. The lack of accurate data on the points mentioned, for the systems studied, makes largely a matter of speculation any present attempt to formulate conclusions regarding the exact contribution of these various factors in determining the final electromotive force exhibited.

Calculation of the heats of reaction for the various cells should agree closely. On this point, using the familiar Gibbs-Helmholtz equation,

$$Q = nF (E - T dE/dT) 0.2387,$$

Stegeman¹ made 2 calculations of the heat of reaction; for cells containing sodium sulfate the error was 0.86%, and for those containing zinc sulfate 0.19%, compared with the value calculated from thermochemical data for the reaction



Similar calculations for the other constant cells should agree closely with the above, indicating that these salts probably do not function in the above reaction, and that it is the only appreciable one occurring.

Conversely, since this Gibbs-Helmholtz equation gives a means of calculating the algebraic sum of the heats of all reactions proceeding when a cell gives a current, if some combination, such as the ones studied, gives an electromotive force appreciably different from those of the constant cells, probably the above reaction is not the only one taking place. Cells containing potassium sulfate, for example, gave an electromotive force considerably higher than that obtained using sodium sulfate, indicating a secondary reaction whose energy is added to that of the primary reaction. The process of this secondary reaction, forming a double salt, is exothermic, and the heat of this reaction corresponds with that calculated from the increase in electromotive force.²

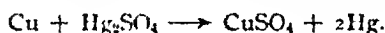
¹ Stegeman, *Dissertation*, Ohio State University, 1917.

² Brönsted, *loc. cit.*

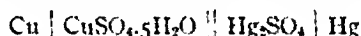
In the case of the cells containing copper sulfate there is evidently some chemical action other than the one between lead and mercurous sulfate, since the electromotive force produced is approximately $\frac{1}{2}$ that of the constant cells. Copper is below lead in the electromotive series, and, therefore, one would expect a displacement of the copper in the copper sulfate by the lead of the amalgam to form more lead sulfate. This reaction would be continuous until equilibrium were reached because of exhaustion of the lead in the amalgam or of the copper sulfate. Because of the comparatively large excess of copper sulfate, the lead should be exhausted first, and the displaced copper should form an amalgam. This would leave as the essential constituents of the reacting system the following arrangement:



In this system would be also the lead sulfate originally added in addition to that formed by the displacement of the copper from some of the copper sulfate. The essential reaction of the cell would now be represented by the equation



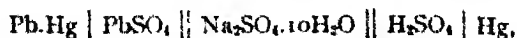
The probable correctness of the latter conclusion seems to be supported by the work of McIntosh¹ on a cell constructed according to the arrangement



For this combination he obtained an electromotive force of 0.3580 volt at 22° as a mean for 4 cells; using his temperature coefficient, this value becomes 0.35605 volt for 25°. The mean value for the authors' 3 cells is about 0.3487 at 25°. It should be borne in mind, however, that McIntosh used a pure copper electrode, while the present electrodes are copper amalgams.² Also he washed his mercurous sulfate with water, which seems a questionable procedure in view of later work with this compound for use in Weston and in Clark cells

Part III. Summary and Conclusions.

A.—A galvanic cell constructed early in 1917 according to the arrangement



in which Pb.Hg represents a saturated amalgam, and PbSO₄, Na₂SO₄.10H₂O, and Hg₂SO₄ represent saturated solutions, has been measured and found to give the same electromotive force as new cells of the same construction, and to have a constant value throughout the present work.

B.—Similar saturated cells have been studied using, in addition to

¹ *J. Phys. Chem.*, 2, 189 (1898).

² Assuming a lead amalgam of 3.1% lead to start, and the complete exhaustion of this lead to displace copper, we should then have an amalgam containing 0.96% copper.

sodium sulfate, the well-defined, soluble sulfates of nickel, cobalt, zinc, manganese, potassium, lithium, magnesium, cadmium and copper. The observations on these cells indicate:

(1) A confirmation, in general, of the work of Henderson and Stegeman on the constancy and reproducibility of cells containing sodium sulfate.

(2) That saturated cells containing the sulfates of nickel, cobalt, zinc, or manganese are substantially as reproducible and as constant as those containing sodium sulfate. This constancy is usually attained within 4 or 5 days, after preparation, and, for the time studied, these cells appear to possess the characteristics necessary for a standard cell.

(3) That the electromotive force of the constant cell seems to be nearly independent of the soluble sulfate used. The values for cells containing sodium sulfate or nickel sulfate practically coincide; while those for cells containing the sulfates of cobalt, zinc, or manganese are very close together, but slightly higher than the first 2.

(4) That saturated cells containing the sulfates of lithium, magnesium, or cadmium are neither reproducible nor constant, although their electromotive force is of approximately the same magnitude as that of the constant cells.

(5) That saturated cells containing potassium sulfate are also neither constant nor reproducible. The mercurous sulfate in them was distinctly hydrolyzed, and their electromotive force was markedly higher than that of the other cells.

(6) That saturated cells containing copper sulfate agree well among themselves but are not constant. Their electromotive force is approximately one-third that obtained for the other cells, indicating that the system contributing the electromotive force has been changed, as a result of the obvious secondary reaction in which the lead of the amalgam displaces copper and the copper goes to make up the amalgam, to that represented by the arrangement,



C.—Unsaturated cells containing the sulfates of sodium, zinc, nickel, cobalt, and manganese have been studied, and the observations on them indicate:

(1) That they are as reproducible as the corresponding saturated cells.

(2) That they give practically the same electromotive force.

(3) That they are constant for a time and then begin to exhibit a decreasing electromotive force.

D.—Two lines of investigation have been conducted in an effort to locate the cause of the unsatisfactory results with saturated cells containing the sulfates of potassium, lithium, magnesium, or cadmium:

a. Unsaturated cells containing the sulfates of lithium, magnesium and cadmium have been studied, and the observations indicate:

(1) That their electromotive force approximately equals that of the corresponding saturated cells

(2) That these cells are equally unsatisfactory.

(3) That the erratic values of the saturated cells are probably not, therefore, the result of the coexistence in the cell of the anhydrous sulfate and a hydrate or of different hydrates, as has been noted in certain Clark cells.

b. Evidence was sought, by means of analytical, microscopic, and thermometric methods, which would indicate whether the unsatisfactory results might be caused by the formation of double salts in the cells. The indications were:

(1) That analytically, there is evidence for the formation of only one double salt, potassium lead sulfate

(2) That microscopically, no conclusions of value are possible.

(3) That thermometrically, the evidence points to the formation of only one double salt, potassium lead sulfate.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY. No 84]

CHEMICAL INDUCTION IN PHOTOGRAPHIC DEVELOPMENT.

I. INDUCTION AND THE WATKINS FACTOR.

BY S. E. SHEPPARD AND G. MEYER

Received December 20, 1919

In previous investigations on the theory of development¹ it was shown that the early stage of development is subject to induction effects, variable from one developer to another, and in each case a function of the bromide concentration.

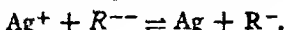
In particular it was shown that the action of bromide as a photographic restrainer consisted primarily in extending the induction period, or delaying the initial precipitation of silver; equations for the velocity of development taking account of the initial retardation were developed. It was pointed out that while this initial induction is greatly extended by bromide that it exists in the absence of bromide, particularly in the case of hydroquinone.² With this developer it becomes more marked on lowering the temperature.

In general, the induction is greater the less the reduction potential of the developer. The reduction potential of a developer was defined from

¹ S. E. Sheppard, *J. Chem. Soc.*, 87, 1312 (1905).

² S. E. Sheppard, *ibid.*, 89, 530 (1906)

the equation for reaction and free energy; taking as the general equation for the chemical change in development,



then the free energy of the reaction is given to a first approximation by the expression (where [] signifies concentration).

$$E = RT \log \frac{[\text{Ag}^+][\text{R}^{--}]}{[\text{Ag}][\text{R}^-]}$$

We can imagine this separated into $RT \log \frac{[\text{Ag}^+]}{[\text{Ag}]}$, which may be termed

the self-reduction potential of the silver ion¹ and $RT \log \frac{[\text{R}^{--}]}{[\text{R}^-]}$, the reduc-

tion potential of the developer. It is evident that the (initial) energy of development will be greater, the higher $[\text{Ag}^+]$, concentration of silver ion, the lower $[\text{met. Ag}]$, concentration of metallic silver. The latter is less, as degree of supersaturation, in the presence of a nucleus, such as the latent image affords; and the supersaturation will be less the smaller the nucleus.² Similarly, for the reducing agent, the further the reaction phase $\text{R}^{--} \rightarrow \text{R}^-$ can go, the greater the reducing energy and the more bromide will be necessary to restrain it.

The Watkins Factor.

The Watkins factorial method of development was introduced by Mr. Alfred Watkins³ in 1894. He found that the time from the pouring on of the developer till the first appearance of the image stands in a constant ratio to the time of development for a given constant density. The Watkins multiplying factor is the quotient of the time of development for this constant density (or constant Hurter and Driffield development factor, γ). The Watkins factor, while showing certain variations for one and the same reducing agent, according to the composition and concentration of the bath, differs very considerably from one reducing agent to another.

The foregoing analysis of the energy factors in development explains why on the whole high reduction potential developers have high Watkins factors and small induction periods. The explanation put forward by Kingdon⁴ that different reducers require different *critical concentrations* to initiate reduction, as accounting for differences in the Watkins

¹ Representing the reaction scheme $\text{Ag}^+ + e \rightarrow \text{Ag met.}$ or the affinity for electrons, in other words, its position in the electrochemical series; inversely of course, its oxidation potential as oxidizer.

² Nuclei below a certain magnitude will have a higher solubility.

³ See A. Watkins, "Manual of Photography." 4th Ed. Chicago, Burke and James. 1908.

⁴ *Phot. J.*, 48 (N. S. 42), 270 (1918).

factor, is obviously contained in this analysis; the *critical concentration* hypothesis is, however, incomplete, inasmuch as it does not take into account other factors which the free energy theory does, as for example, the influence of bromide. It is then of considerable interest for the theory of development that it is possible to alter the Watkins factor for certain developers in the opposite sense to that effected by bromide. The agent we have used for this is a soluble iodide, *e. g.*, potassium iodide in very small concentration. The peculiar "accelerating" effect of such iodides on development was first observed by A. Lainer.¹

Experimental.

The greater number of our experiments were made with a pure silver bromide emulsion. The plates were exposed in an H. & D. type sensitometer and developed under constant temperature conditions. The value taken for the Watkins factor is in general more or less arbitrary, partly from the variable personal element in estimating the "time of appearance," partly from the absence of a fixed convention as to the development factor. The essential point, for the theory of development, does not consist in the absolute values of the Watkins factor, but in this fact that if we take the ratios of the time for some very low constant contrast, *e. g.* (time of appearance, t_a) to the time to develop a definite high constant contrast, *e. g.*, $\gamma = 1.00$) this ratio $t_\gamma = 1/t_a = W$, is characteristic of the developer, but varies widely from one developer to another. For our present work we have taken as Watkins factor $t_\gamma = 0.8/t_a = W$ and obtained the following results:

Concentration of Potassium Iodide 0.100 *N* = 0.0017%.

Treatment	Reducer	Temperature °C	Concentration.	<i>W</i>	Effect on <i>W</i> .
Pretreated	Elon ^a	18	0.5	(30)	×1
		..	0.33	×1
		..	0.25	×1
Pretreated	Glycin ^b	18	1.0	(16)	×2.2
Pretreated	Hydroquinone Caustic	18	×5 to 6

^a *Elon* is methyl *p*-amidophenol sulfate. *Elon* Developer: *Elon*, 5 g.; sod. sulfate, 75 g.; sod. carbonate, 25 g.; water, 1000 cc.

^b *Glycin* is *p*-phenylamido-acetic acid. *Glycin* developer: *Glycin*, 60 g.; sod. sulfate, 120 g.; sod. carbonate, 165 g.; pot. carbonate, 165 g.; water, 1000 cc.

It appears that the "accelerating" effect of very dilute potassium iodide is practically absent with developers such as *elon*, having a high reduction potential and a large Watkins factor, while it becomes very marked with *hydroquinone*, which has a low reduction potential and a small Watkins factor. With the developers above, after a short initial stage, γ is practically unaltered by iodide. With hydroquinone carbonate, however,

¹ A. Lainer, *Phot. Korr.*, 28, 475 (1891); "Eder's Handbuch d. Photographie," 5th ed.

the whole development course is changed, particularly at low temperature, as shown by the following curves and data:

Development with Hydroquinone Carbonate.
Temperature, 8°.

t_0 . Seconds.		Time of development. Minutes.		γ^* .		$\log i$.	
Treated.	Untreated.	Treated.	Untreated.	Treated.	Untreated.	Treated.	Untreated.
6	30	1	1	0.31	0.07	1.05	1.24
6	28	2	2	0.61	0.34	0.90	0.90
6	30	4	4	1.12	0.96	0.88	0.84

Watkins factor: Untreated 7; treated 28.

* γ is the slope of the $D - \log E$ (density: \log_{10} exposure) curve, $\log i$ is the intersection of the straight line portion with the abscissa.

It will be seen that while the hydroquinone carbonate developer at low temperature has a very marked induction, this is largely wiped out by

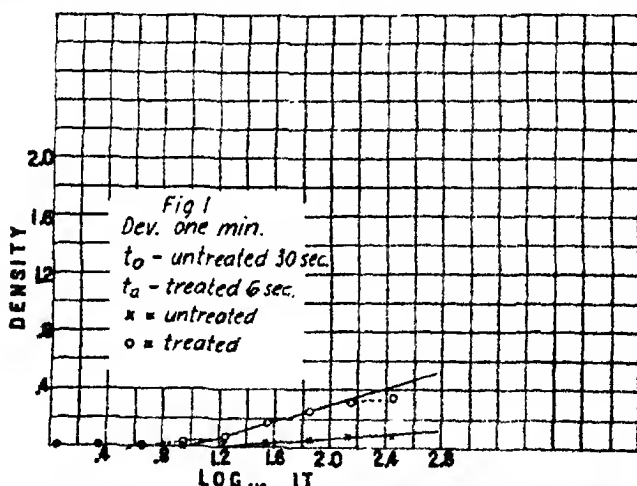


Fig. 1.—Hydroquinone carbonate at 8°. KI placed in developer.

0.0001 *N* potassium iodide solution, giving in fact a developer of quite reasonable developing energy.

Concentration of Potassium Iodide.

The influence of the concentration of the potassium iodide on the initial development energy with hydroquinone is shown in the accompanying curve. It will be seen that over a certain range the effect is at a maximum and then declines rapidly, till permanent restraint on development is brought about.

This latter effect is what we should expect since the iodide reacts with silver bromide forming the less soluble and less reducible silver iodide.

Nature of the Iodide Acceleration.

What is the explanation of the peculiar acceleration at low concentrations? Since the effect can be produced by preliminary bathing with weak iodide solution followed by thorough washing, it is evidently connected with the fixation of small amounts of silver iodide in the silver bromide grains, and not due to any action of the potassium iodide on the developer. The only explanation so far proposed is due to Lippman-Cramer.¹ He supposes that in the conversion of a small fraction of the silver bromide molecules per grain into silver iodide that the halide grain is partly disintegrated or dispersed. The silver nucleus due to exposure is supposed by this to become more effective in accelerating reduction. This hypothesis

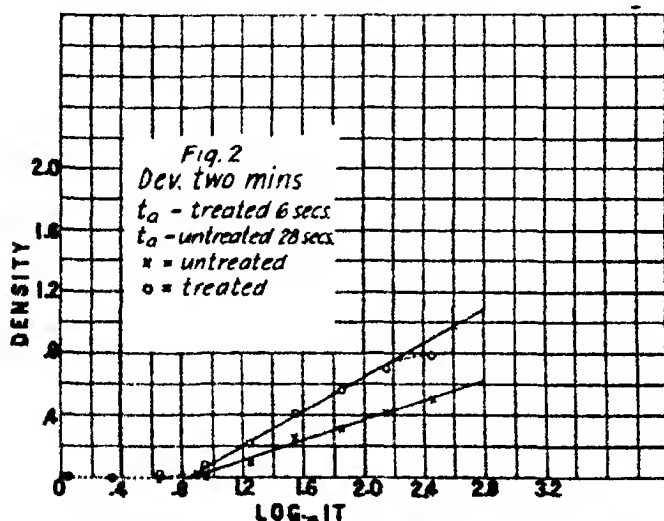


Fig. 2.—Hydroquinone carbonate at 8°. KI placed in developer.

of "unpeeling" the nucleus (*keimblosslegung*) has always appeared very artificial and forced, but has been repeatedly reaffirmed by its author.²

While not readily susceptible of proof or disproof, it does not appear to line up readily with the data brought forward here, i. e., with the quantitative differences in the iodide effect between one developer and another. In particular, the absence of an effect with ferrous oxalate appears inexplicable. It does, however, appear that an alternative hypothesis is possible of considerable higher probability. In a recent letter to the *Photographic Journal*³ it was suggested by one of us that an important phase in development consists in the formation of an intermediate com-

¹ *Phot. Kerr.*, 49, 262 (1912); *ibid.*, 310 et seq.

² Cf. *Phot. Kerr.*, 1912 and later.

³ *Phil. J.*, 89, 136 (1919).

plex between the silver halide and the reducer, and that this unstable intermediate complex undergoes internal decomposition to metallic silver, more or less colloidal, and adsorbed to residual halide, plus discharged oxidized reducer and bromide ions. Now it appears to us that such complex formation at the surface of the silver halide grains is in line with the behavior of potassium iodide. It is well known that silver iodide has a high mordanting action for a considerable number of dyes.¹

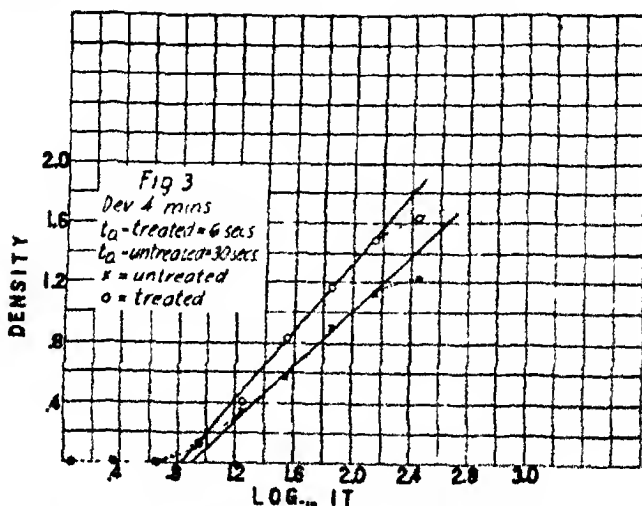


Fig 3 - Hydroquinone carbonate at 8° KI placed in developer

Experiments show that either precipitated silver bromide or silver bromide emulsion acquires greatly increased dye absorption power after a preliminary treatment with dilute potassium iodide solution. On varying the concentration of potassium iodide the vanishing point, i. e., the lowest concentration at which a difference in absorption could be observed between untreated and treated silver bromide is not so low as for its action on development, but this was not to be expected, since development is an extremely sensitive reaction. The results obtained are shown in the following:

ABSORPTION OF DYE (SAFRANINE) ON PRECIPITATED SILVER BROMIDE.

Conc potassium iodide solution
N

0.01

0.002

0.001

0.0005

Excess for treated over untreated

Strong excess

Marked excess

Definite measurable excess

No noticeable difference

1. Cf. A. Traube, *Zeits. Physik. Chem.* 10, 1 (1884).

In these experiments 9 g. of precipitated silver bromide was first treated with 100 cc. of the potassium iodide solution, then with 50 cc. of 1 : 20,000 dye solution, the residual strength of dye in the solution being compared colorimetrically with a blank on untreated silver bromide.

Nature of the Complex Formation.

Supposing complex formation between the silver halide and the developer to be an essential preliminary to development, then this may be viewed in more than one way. First, it may be regarded as a simple excess surface concentration or *adsorption*, not necessarily involving chemical combination with the silver halide. The view that such adsorption plays an important part in development has already been expressed by W. D. Bancroft. In this case, adsorption would act chiefly by increasing the

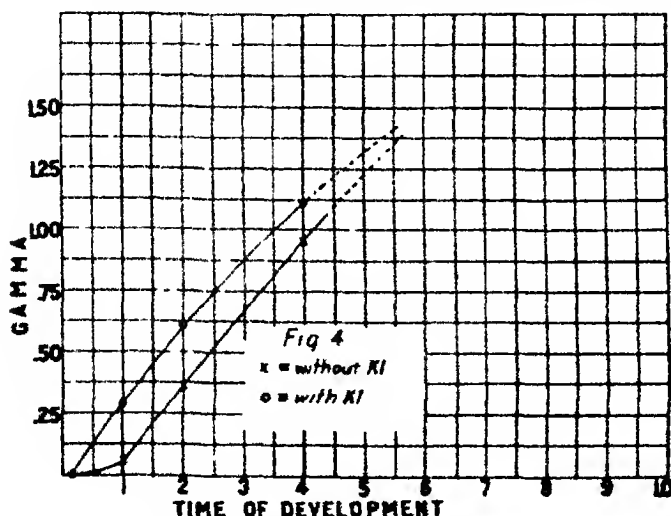


Fig 4.—Hydroquinone carbonate at 8°. KI placed in developer.

local concentration of reducer. If, however, Langmuir's¹ view is correct, that all adsorption is due to chemical (valence) forces then the complex formation will consist essentially in actual chemical combination of the surface silver halide molecules with molecules of the reducer, the valences of the surface molecules of the solid halide being less saturated than those of the interior. The nature of this combination cannot be indicated definitely at present. Thus it might be a combination primarily between the silver cation and the reducer anion, forming a salt-like body, like silver erythrosinate; this body then breaking down in the presence of a nucleus for silver. An example of this in homogeneous solution is shown in the case of silver sulfite. If this is redissolved in excess of sodium sulfite, the

complex silver sulfite anion is comparatively stable at temperatures below 60°. Above this, decomposition, with precipitation of metallic silver, rapidly takes place. If now colloid silver be added to the stable solutions at lower temperatures, decomposition is at once set up and continues rapidly. The colloidal silver behaves here like the latent image in development. It is, however, equally possible that the complex formation is between the un-ionized free base of the organic reducer and the silver halide, forming a stable complex which, however, in presence of alkali (hydroxyl ions) undergoes rearrangement, *viz.*, pseudo-acid formation, salt formation, and ionization. The actual outcome would be then the same as in the former case.

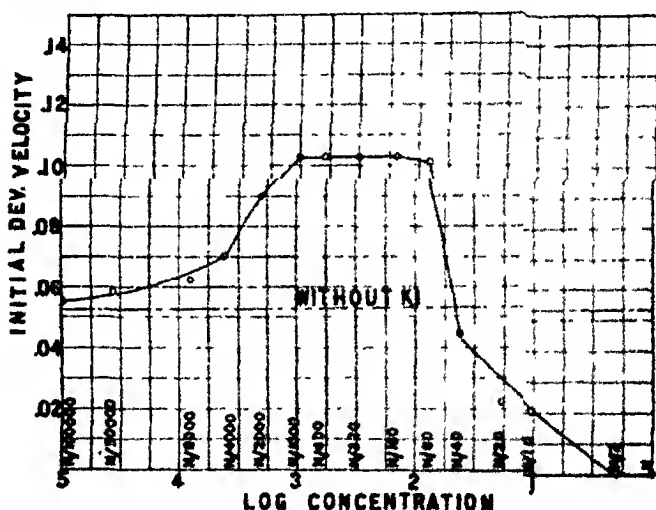


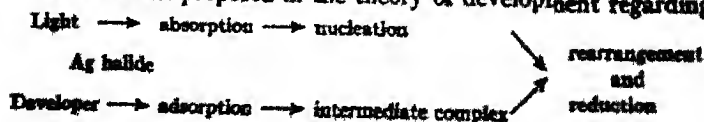
Fig 5.

The fact that the mordanting action of silver iodide is most strongly exerted on basic dyes¹ would favor this interpretation. However, the semi-acid dyes of the phthalein group are also strongly adsorbed.

In any case, the essential matter would be the formation of an intermediate combination, in the circuit of which reaction would take place, with discharge of silver and other oxidation products.

Relation to Silver Grain of Image.

The modification proposed in the theory of development regarding



as essential steps does not contradict the previous theory, but amplifies it on two important points. First, it makes the silver halide grain more emphatically the actual seat of the reaction. It has been suggested by R. Liesegang and Lüppo-Cramer¹ that weak and strong developers in general differ essentially in that the former tend to reduce only the surface of the grain, giving an image of feeble density, usually fine grained and warm toned (ferrous citrate with silver bromide emulsions is a good example), while the latter reduce the whole of the grain, giving more coarse-grained, black-silver image. This effect of the energy of the developer on the dispersity of the image is undoubtedly real, and probably plays a

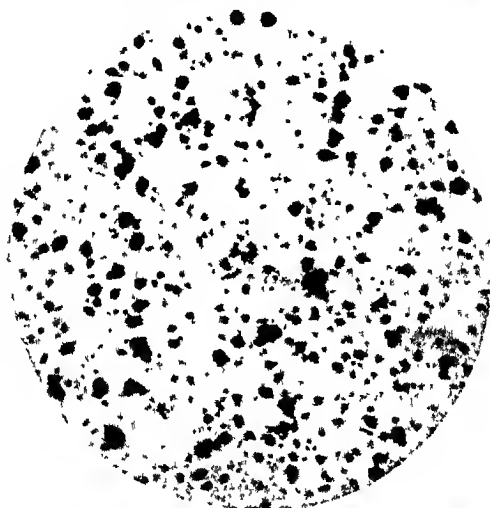


Fig. 6.—Photograph of log caused by dil potassium iodide solution. Mag. 600.

considerable part in the difference of resolving power with different developers.²

If adsorption of the organic reducer is correlated with its reduction potential, increasing with the latter, Bancroft's theory³ that adsorption favors peptization of the solid phase, or adsorbent, indicates a preliminary reason for the change of dispersity of the image with energy of the reducer. Or, again, if adsorption involve formation of an intermediate complex, interfacial to the halide grain and the solution, the lability of this will depend upon the reduction potential of the reducer. This involves a greater velocity of decomposition of the complex, higher dispersity of the silver reduced, and greater mechanical strain on the silver halide

¹ *Kolloid-Z.*, 9, 290 (1911).

² K. Hume, "Photographic Resolving Power," *J. Am. Optical Soc.*, 1, 119 (1912).

grain attacked. The general scheme of development which suggests itself from these considerations at this stage may be outlined as follows, bringing out the essential colloid chemical factors of the process:

Dynamics of Development.

The scheme given is only intended to roughly indicate the interaction of physical and chemical factors.

In particular, while the relation between diffusion of the developer and chemical reactivity determines the "penetration" coefficient, the relation of the "adsorption" to the chemical constitution and reactivity apparently determines the "dispersity" of the image, i. e., an influence of the developer on the grain of the image.

		Remark
a.	Swelling of gelatine film.	The swelling increases the total diffusion path, but lowers the resistance.
b.	Diffusion of developer solution.	Diffusivity increases on either side of neutral point.
c.	Adsorption of reducer to silver halide grains.	
	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p>↓</p> <p>Weak, gives grain surface development.</p> <p>(Pectization) →</p> <p>Weak colored image, fine grain.</p> <p><i>Example.</i></p> <p>Ferrous citrate; acid pyrogallol.</p> </div> <div style="text-align: center;"> <p>↓</p> <p>Strong, volume development</p> <p>(Peptization) →</p> <p>Strong black image, coarse grain.</p> <p><i>Example.</i></p> <p>Normal developers.</p> </div> <div style="text-align: center;"> <p>↓</p> <p>(Solution)</p> <p>"Physical" development, strong, somewhat colored image, fine grain.</p> <p><i>Example.</i></p> <p><i>p</i>-Phenylene - diamine, heavily bromided developers; D. O. P. developers with chlorobromide emulsions.</p> </div> </div>	

Actually, of course, these separately indicated phases of the process overlap and interact. Further, we have only noted here the *direct*, as distinguished from the *reversing* factors of development. The complications involved in the pure chemical reactions, and the regressive effects consequent on resorption of reaction products, while already noticed in part, require much further analysis.

Direct proof of adsorption of organic developers to silver halides under development conditions is difficult owing to the ensuing reactions of decomposition. Experiments to this end are in progress; meanwhile the

ternal evidence are submitted. It is probable that the restraining effect of pyrogallie acid in high concentrations is closely connected with the foregoing considerations.

The extension of the action of potassium iodide to physical developers, as noted by Lüppo-Cramer, is equally in agreement with the view suggested here, although complicated by the facts noted in the next section.

Fogging Action of Iodide.

With most of the developers tried, working with pure silver bromide plates, including hydroquinone at low temperatures, all strengths of potassium iodide from 0.0001 *N* to 0.01 *N* gave on short contact with the emulsion and subsequent washing pronounced fog, consisting of black-silver grains similar to those developed from exposure to light. This fogging action is not primarily connected with acceleration of development, since it was observed with ferrous oxalate, where practically no "development acceleration" occurs. As it appeared possible that the trace of silver iodide formed was acting as a nucleus¹ the following experiment was made. A silver-bromide plate was spotted with 0.0001 *N* potassium iodide solution, fixed in hypo and washed. These spots were then developed in a pyro-citric-acid-silver developer, when they developed up a strong image (see Fig. 6). The photomicrograph shows that the image is comparatively coarsely grained, quite different from the grainless stains frequently obtained on physical development. Hence, it appears probable that the iodide fog is a nucleus infection. It appears considerably more variable than the development acceleration, and less evident with bromo-iodide emulsions. The part played by this in connection with actual development acceleration is being taken up in connection with other development "promoters," as thiosulfate, potassium ferrocyanide, and thiocarbamide.

Lüppo-Cramer² notes that "fog is accelerated by the action of dilute potassium iodide solutions," *i. e.*, he considers it intensifies original fog nuclei just as it does exposure nuclei. Although this no doubt takes place (but not by *keimblosslegung*) there is an independent fogging action, as shown by the effect with developers not showing development catalysis.

Summary.

1. The Lainer effect, acceleration of development by dil. solutions of iodides, has been investigated, and shown to affect chiefly organic developers of low reduction potential such as hydroquinone.

2. It is shown that the principal effect is to overcome the induction with such organic developers, consequently increasing the Watkins factor.

¹ Similarly to colloidal gold as described by one of us in "Investigations on the Theory of the Photographic Process," p. 208. Longmans, Green and Co., London, 1907.

3. The effect is ascribed to increased adsorption and complex formation between silver halide and developer. The bearing of this on the theory of development is discussed.

4. In addition there is a fogging action of dilute potassium iodide solutions on silver bromide emulsions, which is ascribed to nucleus infection of the grain.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE ORIENTATION OF MOLECULES IN SURFACES, SURFACE ENERGY, ADSORPTION, AND SURFACE CATALYSIS.

V THE ADHESIONAL WORK BETWEEN ORGANIC LIQUIDS AND WATER.¹

BY WILLIAM D. HARKINS, GEORGE L. CLARK AND LATEROP E. ROBERTS.

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In 1913 Hardy¹ showed that the magnitude of the work done by the attraction between the surfaces of an organic liquid and water during their approach to form an interface, is characteristic for a number of classes of organic liquids. Later Harkins, Brown, and Davies² found that whenever the organic liquid contains polar groups in its molecules, this work is very much larger than when they are absent; so much higher that the data made it evident that at the interface such polar groups as $-\text{OH}$, $-\text{COOH}$, $-\text{CHO}$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{SH}$, $-\text{NH}_2$, $-\text{NHCH}_3$, $-\text{NCS}$,
 \cdot $\begin{array}{c} \text{H} \\ | \end{array}$
 $-\text{COR}$, $-\text{COOM}$, $-\text{COOR}$, $-\text{NO}_2$, $-\text{C}=\text{CH}_2$, $-\text{C}\equiv\text{CH}$, or groups which contain oxygen, nitrogen, sulfur, iodine, bromine, chlorine, double or triple bonds, turn toward the water. The work of Langmuir³ indicates a similar orientation in monomolecular surface films of organic substances. A theory of heterogeneous equilibrium worked out by Harkins and King⁴ indicates, however, that the orienting forces in the case of such *monomolecular* organic films are in general more powerful than those at the surface of the pure organic liquid, and also greater than those acting on the organic molecules at the interface with water. From the standpoint of the theory

¹ Practically all of the data in this paper were determined during the years 1914-17 or earlier, as the work was interrupted by the war. Some of the data presented here were obtained in this laboratory as early as 1912.

² *Proc. Roy. Soc. (London)*, **88A**, 303-33 (1913).

³ *THIS JOURNAL*, **39**, 354-64 (1917); also Harkins, Davies and Clark, *ibid.*, **39**, 541-96 (1917).

⁴ *Met. Chem. Eng.*, **15**, 468 (1916); *THIS JOURNAL*, **39**, 1843-1906 (1917); *Proc. Nat. Acad. Sci.*, **3**, 251-7 (1917).

of Harkins and King it is, therefore, not to be expected that the indications of orientation will be so marked at interfaces as they are in thin films. However, the evidence obtained at interfaces is more extensive and more varied in its nature.

Table I presents data for the work of surface attraction between water and about 70 organic liquids. In this table the first column gives the name of the substance and the formula; the second (γ), the free surface energy of the organic liquid, the third ($W_A/2$) gives half of the adhesional work per sq. cm. for comparison with Col 2; the fourth (γ_i), the interfacial free energy; the fifth (W_A), the surface adhesion, all in ergs per sq. cm. The sixth column gives the initial of the investigator, and the seventh, eighth and ninth the densities of the pure organic liquids and those of the 2 phases after mixing.

The data in this table are of considerable value in the study of the orientation of molecules in interfaces, and of the characteristics of polar and of non-polar groups in organic compounds. It will be shown later that they are also fundamental in connection with adsorption and surface catalysis. In order that the meaning of the data in terms of cohesion and of adhesion may be appreciated it is essential to present a mechanical illustration. Imagine a bar of solid with a cross section of one sq. cm. If this bar could be pulled *without a lateral compression* until it breaks at a plane perpendicular to its length, the work necessary to pull the bar apart would be equal to 2γ , or twice the free surface energy per sq. cm. of the solid. Thus 2γ may be called the *cohesional (or tensile) work* for a bar of unit cross section. Col. 2, in Table I, gives the value of the free surface energy (γ), which may best be considered in connection with the other data, as half the cohesional work, or γ is equal to $W_C/2$. For comparison with these values the third column (3) gives the values for $1/2$ the adhesional work between the organic substance and water ($W_A/2$). The adhesional work is that which is done by the surfaces of 2 different liquids when one sq. cm. of one approaches the same area of the other. It is the work which would be used up in pulling apart a bar of unit cross section, one end of which consists of one liquid and the other end of the other, if the break could be made at the junction of the two liquids in such a way that they are entirely separated. Thus $W_A/2$ which refers to adhesion, is entirely comparable with $W_C/2$, which is the free surface energy of a liquid, which in turn is numerically equal to the surface tension of the liquid. It will be shown in other papers by Harkins that the adhesional work and energy are related to the heat of adsorption and the heat of wetting, and that the equations are very simple.

So far as this table alone is concerned, columns giving the values of the cohesional work (2γ) and of the adhesional work (W_A), would undoubt-

TABLE I.—THE WORK DONE WHEN ONE SQ. CM. OF THE SURFACE OF AN ORGANIC LIQUID APPROACHES ONE SQ. CM. OF A WATER SURFACE TO FORM AN INTERFACE, TOGETHER WITH THE SURFACE TENSIONS AND INTERFACIAL TENSION.

1. Substance and formula.	2. $\frac{71}{W_A}$ or $\frac{3}{W_A/2}$.	3. $W_A/2$.	4. γ .	5. $-\Delta\gamma$ or W_A .	6 Observed.	7. Density pure liquid.	8. Density organic phase.	9. Density aqueous phase.	10.
$t = 20^\circ$. Water = 72.80 ergs. $W_A = -\Delta\gamma$.									
I. Inorganic Compounds.									
Water, H_2O	72.80	72.80	...	145.6	D
IIa. Paraffins.									
Isopentane, $(CH_3)_2CHCH_2CH_3$	13.72	18.44	49.64	36.88	D	9.44
Hexane, C_6H_{14}	18.43	19.99	51.25	39.98	D	9.44
Octane, C_8H_{18}	21.77	21.88	50.81	43.76	D	0.22
Di-iso-amyl (Decane).....	22.24	24.12	46.80	48.24	R	0.72216	0.72253	0.99696	3.76
Higher paraffins (about $C_{14}H_{30}$), containing benzene derivatives 30.83	31.51	40.61	63.02	D	1.36
IIb. Unsaturated Paraffins.									
Trimethyl ethylene, $\begin{array}{c} CH_3 \\ \diagup \\ C = C \\ \diagdown \quad \diagup \\ CH_3 \quad CH_3 \end{array}$	17.26	26.68	36.69	53.37	D	18.85
IIIa. Primary Alcohols.									
Methyl, CH_3OH	21.7	47.7	...	95.5	50.1
Ethyl, C_2H_5OH	22.4	47.6	...	95.2	50.4
Propyl, C_3H_7OH	23.7	48.2	...	96.5	51.1
Butyl, C_4H_9OH	24.5	48.6	...	97.3	49.1
Isobutyl, $(CH_3)_2CHCH_2OH$	22.8	46.9	1.8	93.8	48.3
Isopentyl, $(CH_3)_2CHCH_2CH_2OH$	24.1	46.2	4.4	92.5	48.2
Octyl, $(CH_2)_7OH$	27.53	45.88	8.52	91.77	D	44.3
IIIb. Secondary Alcohols.									
Methylthetyl carbinol, $CH_3CHOH(CH_2)_5CH_3$	26.52	44.85	9.61	89.71	D	36.67

TABLE I (continued).

1. Substance and formula	2. v_1 or $\bar{\nu}_1/2$	3. $\bar{\nu}_2/2$	4. $\bar{\nu}_3/2$	5. Obs. or $\bar{\nu}_A$	6. Density pure liquid.	7. Density organic phase.	8. Density aqueous phase	9. Density aqueous phase	10. Density aqueous phase
VIII. Esters Containing the $-\text{O}-\text{C}=\text{O}$ Group.									
VIII. Halogen Derivatives.									
Ethyl carbonate, $(\text{C}_2\text{H}_5\text{O})_2\text{C}=\text{O}$	26.31	43.22	12.86	86.25	D	59.94
Methylene chloride, CH_2Cl_2	26.52	35.50	38.31	71.01	C	1.3478	1.3286	1.0018	17.97
Chloroform, CHCl_3	27.13	33.65	32.63	67.30	C	1.485	1.4831	1.0002	13.04
Carbon tetrachloride, CCl_4	26.66	28.07	43.26	56.15	C	1.590	1.5846	1.9972	2.83
Ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$	24.16	32.88	31.20	65.76	C	1.441	1.4463	1.0001	17.44
Ethylene dibromide, $\text{CH}_2\text{BrCH}_2\text{Br}$	38.71	37.48	36.54	74.97	C	2.178	2.1773	0.9991	-2.4
Acetylene tetrabromide, $\text{CHBr}_2\text{CHBr}_2$	49.67	41.82	38.82	83.65	C	2.9620	2.9588	0.9986	-5.69
Isobutyl chloride, $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$	21.94	35.15	24.43	70.31	D	26.46
Ter. butyl chloride, $(\text{CH}_3)_3\text{CCl}$	19.59	34.32	23.75	68.64	D	29.34
Iso-amyl chloride, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Cl}$	23.48	40.42	15.44	80.84	R	0.86962	0.87146	0.9955	33.88
IX. Nitro Compounds and Nitrates.									
Nitromethane, CH_3NO_2	36.82	49.98	9.66	99.96	C	1.1385	1.1288	1.0184	26.32
Iso-amyl nitrate (Note 1)	27.18	...	30.80	69.18	R	0.99710	0.99745	1.0059	42.2
X. Nitrils.									
Acetonitril, CH_3CN	28.4	50.5	...	101.0
Butyronitril, $\text{CH}_3(\text{CH}_2)_2\text{CN}$	28.06	45.24	10.38	90.48	R	0.79040	0.79436	0.99201	34.36
Isobutyronitril, $(\text{CH}_3)_2\text{CHCH}_2\text{CN}$	26.03	43.34	14.14	84.69	R	0.79106	0.79394	0.99622	32.63
XI. Amines.									
Diisopropyl amine, $(\text{C}_3\text{H}_7)_2\text{NH}$	22.54	46.84	1.66	93.68	R	0.73853	0.81620	0.98844	48.60
Di-isobutyl amine, $((\text{CH}_3)_2\text{CHCH}_2)_2\text{NH}$	22.05	43.28	10.28	84.57	R	0.74428	0.74763	0.99680	40.47

XII. Aromatic Hydrocarbons.

Benzene, C_6H_6	28 86	33 31	35 03	66 63	8.91
Toluene, $C_6H_5(CH_3)$	29 89	33 31	36 06	66 63	6.84
<i>o</i> -Xylene, $C_6H_4(CH_3)_2$	29 89	33 31	36 06	66 63	R	0 87810	0 99707
<i>m</i> -Xylene, $C_6H_4(CH_3)_2$	28 72	31 81	37 89	63 63	6.19
<i>p</i> -Xylene, $C_6H_4(CH_3)_2$	28 31	31 68	37 77	63 36	R	0 86444	0 99680
Ethyl benzene, $C_6H_5(CH_2CH_3)$	28 51	31 30	38 70	62 61	R	0 86124	0 99717
<i>p</i> -Cymene.....	28 09	30 24	34 61	66 28	R	0 85618	0 99702

XIII. Halogen Derivatives

Chlorobenzene, C_6H_5Cl	33 08	34 23	37 41	68 47	C	1 057	1 1047	0 9972	2 31
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XIV. Amine Derivatives

Aniline, $C_6H_5NH_2$	42 58	54 80	5 77	109 61	C	1 022	1 0216	0 9990	24 45
Dimethyl aniline, $C_6H_4N(CH_3)_2$

XV. Nitro Derivatives

Nitrobenzene, $C_6H_5NO_2$	43 18	45 26	25 66	90 52	C		1 2012	0 9976	3 76
<i>o</i> -Nitrotoluene, $C_6H_4CH_3NO_2$	41 46	43 53	27 19	87 07	C	1 168	1 1599	0 9972	4.15
<i>m</i> -Nitrotoluene.....	40 99	43 05	27 68	86 11	C	1 168	1 1547	0 9971	4 13

XVI. Aldehyde Derivatives

Benzaldehyde, C_6H_5CHO	40 04	48 66	15 51	97 33	C	1 0504	1 0445	0 9981	17 25
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XVII

Anisol, $C_6H_5OCH_3$	35 22	41 10	25 82	82 20	R	0 99337	0 99270	0 99715	11 76
Phenetol, $C_6H_5OC_2H_5$	32 74	38 07	29 40	76 14	R	0 96474	0 96474	0 99820	10 65

C = Clark. R = Roberts. D = E. C. H. Davies. E = D. T. Ewing.

NOTE 1.—All data were taken at 20°, except those for undecylic acid which were obtained at 25°. The interfacial tension of iso-amyl nitrate was not determined against pure water, but against a 0.177 N KCl solution, since the liquid and pure water have almost identical densities.

NOTE 2.—The density data in the above table are of value, since from them an estimate may be obtained of either the solubility of the organic liquid in water, or of water in the organic liquid.

subject, than the half values given in the table. The purpose in the use of $W_C/2$ and $W_A/2$ is to make these terms directly comparable with the surface tension values given in tables of constants. The most extensive table of this kind was presented in an earlier paper from this laboratory.

The data in this table are in general easy to interpret in terms of the theory that the molecules in a surface or an interface between two liquids are oriented. If the orientation of the organic molecules is considered, it seems self-evident that the effects of such an orientation, and also its extent, depend upon the degree of dissymmetry in the organic molecule. An entirely symmetrical molecule (or atom in the case of monatomic liquids) would not orient at all, but such a molecule or atom probably does not exist. Molecules as symmetrical as those of the short chain saturated paraffins, carbon tetrachloride, etc., would not be expected to show such evidences of orientation as those molecules which may be considered as heavily loaded, from the standpoint of the stray electromagnetic field, at one end of the molecule, and very light, in the same sense, at the other. The table gives evidence that saturated paraffin groups have a small attraction for water, and that groups containing oxygen or nitrogen, hydrosulfide, or any of the other groups specified in the first part of this paper, that is what are termed "polar groups," have a relatively high attraction for water. The orientation has been already considered in connection with similar data obtained in this laboratory, together with the data of Hardy,¹ and this earlier paper should be consulted for the introduction to the discussion of the much more extensive data presented here.

Whenever $W_A/2$ (Col. 3) is greater than $W_C/2$ (Col. 2), then the work of attraction between the organic liquid and the water is greater than that between the parts of the organic liquid itself; that is, the adhesional work is greater than the cohesional work. This is the relation in most cases, but for the following 3 liquids the work due to the cohesional attraction is the greater: carbon disulfide, ethylene dibromide, and acetylene tetrabromide. It is striking that, judging by the formulas, all of these molecules are extremely symmetrical. The difference between these column multiplied by 2, which is equal to $(W_A - W_C)$, or the excess of the adhesional over the cohesional work, is given in Col. 10. Low values of this quantity are obtained in 3 ways: first, as in the case of the "non-polar" paraffins both the adhesional and the cohesional work are low, usually of the order of 40 ergs. per sq. cm.; second, the organic molecule is slightly polar, but the polarity is distributed over a considerable part of the organic molecules, as in the case of benzene and its paraffin derivatives, when both values are somewhat larger (about 60); and third, when a considerable part of the molecule of the organic substance becomes

¹ Harkins, Brown and Davies, *THIS JOURNAL*, 39, 354-64 (1917).

more polar, as in the case of nitrobenzene, and the nitrotoluenes (about 86). The adhesional work becomes much higher than the cohesive work whenever the polar group is in just one part of the molecule, while the rest is non-polar, and particularly when the polar group is at one end of the molecule. Thus the excess of the adhesional over the cohesive work ($W_A - W_C$) is to a considerable extent an index of the total symmetry of the molecule, and indicates how symmetrically the molecules lie in the surface and interfaces.

Consider carbon disulfide and ethyl mercaptan. The cohesive work in the former is much higher, 62.8 instead of 43.6, yet the attraction between water and carbon disulfide (adhesional work = 55.8) is much less than that between water and mercaptan (68.5).

The former is a symmetrical molecule, and the latter is unsymmetrical. The hydrosulfide group is evidently more polar than the divalent sulfur atom, but when the mercaptan lies in contact with the water most of the hydrosulfide groups are turned toward the water, and when they are pulled from it the polarity of the group is evident in the high value of the adhesional work. The =S group, not being so polar, gives a considerably smaller value, which is 12.7 ergs less. However the attraction between the sulfur of carbon disulfide and water, and also that between the sulfur in the different molecules of the carbon disulfide itself, is much greater than the attraction between hydrocarbon groups such as C_2H_5- . Now when a bar of carbon disulfide is pulled apart to make 2 surfaces, sulfur must be pulled away from sulfur, so the cohesive work and also the total cohesive energy are relatively high, the former having a value of 62.76 ergs per sq. cm. However when mercaptan is pulled apart, sulfur ($-SH$) does not need to be pulled from sulfur, but the sulfur turns under the surface, and only the hydrocarbon groups have to be pulled apart, so the work of separation is low (only 43.6). However, the work of separation is not so low as if the sulfur were absent, since what is given above is a static theory, and the kinetics of liquids indicates that some of the hydrosulfide groups will be kept in the surface of the mercaptan, by the kinetic motion of the molecules. A paper by Harkins to be published in a few weeks in the *Proceedings of the National Academy of Sciences* shows that the heat motion of the molecules is an important factor in such cases as this, and also at interfaces. In all previously investigated cases, except when liquid crystals are being transformed in the surface, the heat motion aids in the formation of a surface. The paper will show that in some cases with molecules which are polar at one end and not at the other, the heat motion hinders the formation of the surface, since it hinders the orientation of the molecules.

A comparison of the halogen derivatives is also instructive. The co-

hisional work for carbon tetrachloride, chloroform,¹ and methylene chloride is almost the same (53.32, 54.26, 53.04), but the adhesional work toward water rapidly increases in the order given (56.16, 67.30, 71.0). Here the increasing polarity is not in evidence in the cohesive work but is present in the adhesional work, since when the pure liquids are pulled apart the increase of cohesive work due to an increase of polarity is counterbalanced by the concomitant increase of dissymmetry, which allows the less polar parts of the molecules to be oriented into the surface. At the interface, however, it is the most polar part which is turned into the interface, so the effects add together instead of subtracting. Also the adhesional work for isobutyl and tert. butyl chloride are practically as high as in the case of methylene chloride, since the chlorine is turned toward the water, but the cohesive surface work drops to very low values, 43.88 and 39.18 ergs per sq. cm.

Both carbon tetrachloride and ethylene dibromide give the same value for the cohesive work as for the adhesional work, but, as the number of bromine atoms in the compound increases (acetylene tetrabromide) the cohesive work becomes the higher. These compounds have very symmetrical molecules.

A comparison of isopentene with trimethyl ethylene, and of octane with octylene shows that the introduction of a double bond increases the cohesive work very slightly and the adhesional work very greatly, especially in the latter case, where the double bond is at the end of the molecule. These facts are again exactly in accord with the orientation theory. For octane the cohesive work is 43.54, while for octylene it is almost the same, or 44.66, so the introduction of the double bond has little effect. The values of the adhesional work for octane is practically the same as that for the cohesive work, but the addition of the double bond in octylene raises the value by about 60%.

Substances of the type of the primary alcohols, mercaptans, acids, amines, nitriles, nitro compounds, or derivatives with double or triple bonds at one end, may be classified as compounds with polar-non-polar molecules of the general formula \bigcirc —, where the \bigcirc represents a polar and — a non-polar group. While the polar group may have either a higher or a lower weight than the non polar, the action of the molecule in a liquid is analogous to that which would be obtained in a system of models made up with a heavy and a light end, if the models could be taken out of an external gravitational field, and turn freely under the action due to the mutual gravitational field, the chief difference being that the gravitational field is much less intense than the elec-

¹ The molar internal latent heat of vaporization for carbon tetrachloride is almost identical with that of chloroform, 7570 for the former and 7455 for the latter at 0°. The error in the determinations is greater than this difference.

tromagnetic field at small distances, but dies off much more slowly. At the surface of a closely crowded aggregation of such models in motion the heavy ends would, on the average, be very much more likely to turn inward toward the body of the aggregation, but at the interface between such an aggregation and a second set of models consisting of weighted parts alone, these models would turn toward the weighted system. We may thus speak of the electromagnetically light and heavy ends of the molecules of this type in place of the non-polar and polar ends. The interpretation of the data presented in this paper may easily be made by the reader on the basis of such a set of models. For molecules of the type under discussion it will be seen that the cohesive work is always low, and the adhesive work is toward water always high. The work of this laboratory indicates that the same relations hold toward mercury¹ except that in this case bromine and especially iodine act as if they are much more heavily loaded in this sense than oxygen or nitrogen, which is just the opposite of their relative order toward water. Thus oxygen or nitrogen, and especially bromine and iodine, turn toward the mercury.

The data of Col. 10 show the excess of the adhesive work toward water over the cohesive work of the organic substance. This is nearly zero for most of the saturated paraffins but increases to about 19 ergs for trimethyl ethylene with its partly surrounded double bond, or by 28 ergs for octylene. In the case of the alcohols, and dipropylamine the excess rises to 50 ergs, while it is 60 ergs for ethyl carbonate and a symmetrical dichloro-acetone, 45 ergs for normal acids and ether, and from 32 to 40 ergs for ketones. Thus all of these liquids have a much smaller surface attraction for themselves than for water. Hydrocarbons of the benzene series and nitro and chlorobenzene on the other hand give low values of $W_A - W_C$, and in this respect are similar to the paraffins. The values for anisol and phenetol rise to 11, for benzaldehyde to 17, and for aniline to 24.

The solubility of the organic substance in water increases in general as $W_A - W_C$ increases, though this, it is apparent, is only one of the factors. According to the orientation theory this term relates mostly to the attractive forces around the more polar end of the molecule, so it is to be expected that the extent and polarity of the rest of the molecule are also important factors, as is evident from the data. The application of this theory to solubility has already been discussed in the previous papers of this series, though the values of $W_A - W_C$ are given here for the first time.

The calculations in this paper are based on the simple thermodynamic equation of Dupré, which may be expressed

$$W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{12}$$

¹ Work of Dr. E. H. Grafton and W. W. Ewins.

where $-\Delta\gamma$ is the decrease of free energy when 2 unlike or 2 like surfaces meet. The equation of Harkins gives the total energy change when the surfaces meet as follows:

$$E_A = -\Delta E_S = \gamma_1 + l_1 + \gamma_2 + l_2 - (\gamma_{12} + \gamma_{12})$$

where E_A is the total energy of adhesion, E_S , the total surface energy, and l is the latent heat of the surface. This equation is more closely related to the molecular attractions than that of Dupré, but its application will be discussed in another paper, which will give the experimental values.

These equations may easily be transformed so as to give the heat of adsorption, and the energy quantities are those which are of importance in surface or heterogeneous catalysis, or what is often termed contact catalysis. The next papers of this series will treat the following subjects: the change of molecular kinetic to molecular potential energy, the steps in the process of vaporization, the attraction of mercury for organic liquids and water, the compression of liquids by adsorption, the absorption of liquids and gases in charcoal, heats of adsorption, and the adsorption of organic acids and alcohols containing from one to ten carbon atoms on a water surface, the adsorption of salts, adsorption at the interface between hexane and water, the hydrolysis of a soap in the surface film, and negative surface energy. These papers are now largely completed.

Summary.

1. This paper gives new determinations of the interfacial tension between organic liquids and water, together with the surface tension of the pure liquid for 34 carefully purified organic liquids, together with similar data for 24 liquids as previously determined in this laboratory. The only determinations available when the work of this laboratory was begun in 1912, consisted of those on 4 liquids by Antonow and on 20 liquids by Hardy. That the measurements made in this laboratory are much more accurate is due to the painstaking work of Dr. F. E. Brown and Dr. E. C. H. Davies on the corrections involved in the use of the drop weight method. The earlier work has already been summarized in a former paper. A knowledge of such interfacial relations is of fundamental importance in the study of (1) colloids, as in physiological work, (2) adsorption, (3) the spreading of liquids on surfaces, (4) adhesion, including flotation, (5) surface structure, (6) surface catalysis, and (7) lubrication.

2. The data give much evidence in favor of the theory that the molecules in interfaces are oriented. This is in accord with the theory developed both by Langmuir and by Harkins and his co-workers. That there is such an orientation was first suggested by Hardy, but he did not present evidence in favor of the idea. However, he has not been given sufficient credit for his beautiful work on surfaces and interfaces.

3. The paper gives values for the work necessary to pull apart a column of an organic liquid, which is equal to twice the free surface energy, and is termed the cohesive work for a bar of unit cross section. Values are also given for the adhesional work against water. This is the work done when one sq. cm. of an organic liquid approaches a similar area of water. This is one of the important factors in determining solubility in water, and the values are also an index of the polar nature of the most polar part of the organic molecule.

4. The evidence presented may best be considered by an example, which is only one of the many cases included in the data. From the formula it may be considered evident that carbon disulfide has an extremely symmetrical, and mercaptan ($\text{CH}_3\text{CH}_2\text{SH}$) a very unsymmetrical molecule. Now it takes much more work to pull apart a bar of carbon disulfide than of mercaptan, that is the cohesive work is much higher in the former case (62.8 instead of 43.6), yet the work of attraction or the adhesional work between water and carbon disulfide is much less (55.8) than it is between water and mercaptan (68.5). These remarkable facts are very simply explained in the paper from the standpoint of the orientation theory. The data show that the presence of a polar group in any part of an organic molecule, no matter how large the non-polar part of the molecule may be, increases very greatly the attraction of the organic liquid for the water, which is strongly in support of the orientation theory. Thus the attraction between octane and water is relatively small, the adhesional work being only 43.76 ergs. The octane molecule contains 8 carbon and 18 hydrogen atoms, or 26 atoms in all, yet the introduction of only one oxygen atom at the end of the chain more than doubles the adhesional work, and increases it to 91.77 ergs. The similar introduction of one oxygen atom into isopentane increases the adhesional work toward water from 36.9 to 92.5, or a remarkable increase of 150%. The substitution of an amine group for a hydrogen atom at the end of the chain causes an increase of the same magnitude, as does the substitution of $-\text{COOH}$, $-\text{CN}$, $=\text{CO}$, or any similar groups. The great magnitude of the effect, when it is considered that the addition of one atom to 26 causes an increase of 132%, is remarkably strong evidence that the oxygen is turned toward the water.

5. It is found that the only 3 cases out of 58 is the cohesive work of an organic liquid greater than its adhesional work toward water. The liquids are carbon disulfide, ethylene dibromide, and acetylene tetrabromide. The excess of the adhesional over the cohesive work increases as the symmetry of the molecule decreases. This is also very strong evidence in favor of the orientation theory.

6. The data indicate that the benzene series hydrocarbons are considerably more polar than the paraffin hydrocarbons. Aniline is found to

be extremely polar in comparison with most of the organic liquids. The polar characteristics of the benzene derivatives are distributed much more over the whole molecule than is the case with the paraffin derivatives.

7. Attention should be called here to an error which is sometimes made in connection with the orientation theory, which is that the total surface energy, and the free surface energy, or the surface tension, are all due to the orientation of the molecules. This is just the opposite of the truth, since the surface energy is due to the stray surface field, and this field is decreased, and not increased, by the orientation. The general law for surfaces as presented by Harkins, Davies and Clark is: If we suppose the structure of the surface of a liquid to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapor phase, and at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt. This last statement expresses a general law of which the adsorption law is only a special case. If the molecules are monatomic and symmetrical, then the orientation will consist in a displacement of the electromagnetic field of the atom. Since it is the *free* energy which is decreased by the orientation, thermodynamics tells us that the orientation will take place of itself.

The work of this paper, as well as that of the 4 earlier papers of this series, was made possible by a grant made in 1911 from the C. M. Warren Fund of the American Academy of Arts and Sciences.

CHICAGO, ILLINOIS

[PLANT PHYSIOLOGICAL AND FERMENTATION INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE RELATION BETWEEN THE TOTAL ACIDITY, THE CONCENTRATION OF THE HYDROGEN ION, AND THE TASTE OF ACID SOLUTIONS.

BY R. B. HARVEY.

Received January 16, 1920

In some determinations of the hydrogen ion concentrations of various fruits, including apples and tomatoes, the author found that sour varieties gave nearly the same value as did less sour varieties. The small variation in the hydrogen ion concentration of 30 varieties of tomatoes from P_H 4.148 to 4.565 seems insufficient to account for the difference in taste. This suggested the question: "What do we taste in acid solutions, hydrogen ion concentration or total acidity?"

Opinions of various persons differs, but most seem to believe that the concentration of hydrogen ions is the important factor. Some work by

Kahlenberg¹ and Richards² indicates that there are factors of importance other than hydrogen ion concentration, but no definite relation of the factors is given. Crozier³ suggests that the potentially ionizable hydrogen is a factor as well as the actual hydrogen ion concentration.

By making buffer solutions of different values of hydrogen ion concentration one can then obtain dilutions with the same hydrogen ion concentration but differing widely in total acidity. The same total acidities can also be produced at different hydrogen ion concentration values. The hydrogen ion concentration of an acetate-buffer mixture depends upon the ratio of acetic acid to sodium acetate, and not upon the total acetate ion present.

With the assistance of a number of persons in the Bureau of Plant industry, a comparison was made between the tastes of sodium acetate and acetic acid buffer mixtures at different hydrogen ion concentrations and at different total acidities for each hydrogen ion concentration. The range covered was from solutions almost too sour to be tolerated down to practical neutrality of taste. The acid taste of the buffer solutions was expressed in terms of the normality of hydrochloric acid of the same degree of sourness. For hydrochloric acid the dissociation into hydrogen and chlorine ions is practically complete for the dilutions which can be tasted without injury, 97% for $N\ 0.025N$.⁴

The hydrogen ion concentration and total acidity of hydrogen chloride solution is, therefore, practically the same. Hydrochloric acid was selected on account of its almost complete dissociation, its lack of oxidizing or other disturbing properties possible in other acids. Some confusion was experienced by nearly all the experimenters on account of slight differences in flavor of the 2 different acid solutions. Hydrochloric acid has a faintly bitter taste while acetic acid tastes somewhat aromatic. This is evidently due to the negative radical and would be difficult to eliminate. This confusion was noticed mostly in the more acid solutions. The dilutions were made with redistilled water and this was found to be confusing in the higher dilutions on account of its insipid taste. Considerable difficulty was found in remembering the taste of a solution, but by repeated alternation 5 persons usually selected the same or nearly the same standard solution without knowing the dilutions given for the trial. It

¹ Louis Kahlenberg, "The Action of Solutions on the Sense of Taste," *Bull. Univ. Wisconsin*, 25; *Science Ser.*, 2, No. 1, 1-31 (1898); "The Relation of Taste of Acid Salts to Their Degree of Dissociation," *J. Phys. Chem.*, 4, 33 (1900); "The Relation of Taste of Acid Salts to Their Degree of Dissociation, II," *ibid.*, 4, 333 (1900).

² T. W. Richards, "The Relation of the Taste of Acids to Their Degree of Dissociation," *Am. Chem. J.*, 20, 121-126 (1898).

³ W. J. Crozier, "Taste of Acids," *J. Exp. Neurology*, 26, 453-462 (1916).

⁴ Landois-Börnstein, "Physikalisch-Chemische Tabellen."

was found that experience was gained so that one could more accurately estimate the acidity after a few trials.

The sourness of an acetate-buffer solution, measured as equivalent to a solution of hydrochloric acid in which the hydrogen ion concentration and total acidity are the same, is a function of 2 independent variables, the hydrogen ion concentration of the buffer solution and the total acidity of the buffer solution.

By plotting the negative logarithms of the various ion and total concentrations expressed in equivalents per liter, on logarithmic 3 dimensional Cartesian coordinates, the graph modeled in Fig. 1 was obtained, showing the relative values of the total acidity, the hydrogen-ion concentration, and the sourness of the solution.

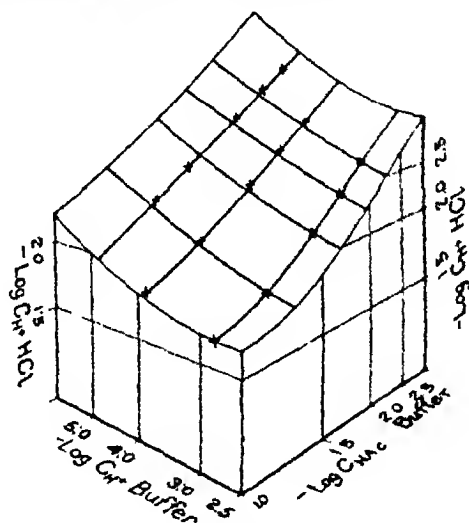


Fig. 1.

From these values it appears that the total-free acid of the solution is a factor as well as the hydrogen ion concentration. It is desirable, therefore, in determining the acidity of acid foods to give both of these values in order that their desirability as edible products can be determined.

In the ingestion of such acid foods as tomatoes or citrous fruits the tendency to produce hyperacidity is, therefore, dependent also upon the total acidity or quantity of acid ingested and not necessarily upon the hydrogen-ion concentration alone. Although it alters the taste, the addition of sugar changes neither the hydrogen-ion concentration nor the total acidity of a solution.

WASHINGTON, D. C.

HYDRATION AS AN EXPLANATION OF THE NEUTRAL SALT EFFECT.

BY JOHN ARTHUR WILSON.

Received January 19, 1920

A mass of experimental data now available seems to indicate that the addition of sodium chloride to an acid solution results in an increase in hydrogen-ion concentration, whereas adding it to an alkaline solution causes an increase in concentration of the hydroxide ion.¹ This is of very great importance in the manufacture of leather, although probably not more so than in other fields of chemistry.

An interesting practical example of this property of salt is furnished by a series of experiments in chrome tanning recently carried out by the writer. A commercial chrome liquor (a solution of basic chromic sulfate and sodium sulfate) diluted to contain 17 g. of chromic oxide per liter was found to be capable of completely tanning certain pickled² calfskins in less than 2 days without any addition of alkali. A piece of chrome leather is considered fully tanned when it will remain apparently unaltered in boiling water for 5 minutes. In tanning successive lots of skins with this liquor, no difficulty was experienced in maintaining conditions so nearly constant that no difference could be detected either in the rate of tanning or in the properties of the resulting leather. The experiment was then repeated with all conditions exactly the same as before except for the addition of one lb. of sodium chloride per gallon (120 g. per liter) of chrome liquor. Measurements with the hydrogen electrode showed that an increase of about 50% in hydrogen ion concentration resulted from this addition of salt. After the skins had been in the liquor for 7 days, they were still not tanned and it was necessary to add a considerable amount of alkali to bring about complete tannage. A very similar effect is produced by adding hydrochloric acid instead of salt.

The effect of sodium chloride upon alkaline solutions is shown by adding salt to a lime liquor, which consists of a solution kept saturated with calcium hydroxide by means of a large excess and containing a comparatively small amount of sodium sulfide. The function of this liquor is to destroy the Malpighian layer of the epidermis of the skins so that the hair may simply be rubbed off by working on a suitable machine. Adding salt to such a liquor was found to increase the plumpness of the skins and to cause the hair to slip somewhat more easily. This same effect is produced by the addition of sodium hydroxide.

¹ Poma, *Z. physik. Chem.*, 88, 671 (1914); Arrhenius, *ibid.*, 31, 197 (1899); Harned, *This Journal*, 37, 2460 (1915); Fales and Nelson, *ibid.*, 37, 2769 (1915); Thomas and Baldwin, *ibid.*, 41, 1981 (1919).

² The pickling process consists of subjecting unhaired skins to a bath of sulfuric acid and sodium chloride of definite strength until equilibrium is established.

The chrome tanning experiments noted above were a continuation of a series of simpler experiments by Wilson and Kern,¹ of which the following is typical. 0.1 *N* sodium hydroxide was added to 10 cc. of a filtered chrome liquor, with suitable agitation, until the first permanent turbidity appeared, due to precipitation of basic chromic salts, the amount required being 3.7 cc. To another portion of 10 cc. was added 0.04 gram molecule of sodium chloride; in this case 6.8 cc. of the standard alkali was required to start precipitation. Repeating the experiment, using in each case 10 cc. of the chrome liquor and 0.02 gram molecule of added salt, Wilson and Kern found different salts to have very different degrees of effectiveness in preventing precipitation, the order being $\text{KCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{MgCl}_2 < \text{MgSO}_4 < \text{Na}_2\text{SO}_4 < (\text{NH}_4)_2\text{SO}_4$. The liquor containing potassium chloride required only 4.0 cc. of 0.1 *N* sodium hydroxide to start precipitation against 11.6 cc. for ammonium sulfate.

The order of these salts led Wilson and Kern to the conclusion that the effect was probably due to hydration of the added salt. Chrome liquors are all decidedly acid in reaction, and, if the added salt becomes hydrated at the expense of the solvent, the ratio of moles of acid to moles of solvent, and consequently the activity of the acid, will be increased, the more so the greater the degree of hydration of the added salt.

This explanation was regarded as sufficient until Thomas and Baldwin² proved by electrometric measurements that while chlorides actually do increase the hydrogen-ion concentration, not only of chrome liquors but of pure acid solutions as well, sulfates behave very differently, generally lowering the hydrogen-ion concentration, just the reverse of what might have been expected from the results of Wilson and Kern.

One remarkable feature of the results of Thomas and Baldwin is that when the logarithm of the concentration of hydrogen ion is plotted against concentration of added salt in the case of the alkali chlorides, the curves are apparently straight lines, of the general formula

$$\log [\text{H}^+] = \log a + bm \quad (1)$$

where *b* is a constant, *a* the hydrogen-ion concentration with no added salt, and $[\text{H}^+]$ the hydrogen-ion concentration in the presence of *m* moles per liter of added salt.

Since all that remained to make this equation a valuable instrument for the rapid estimation and control of the hydrogen-ion concentrations of pickle liquors was the determination of *b* for various strengths of acid, the writer, assisted by Mr. Rudolph Olson, repeated the work of Thomas and Baldwin for other strengths of sulfuric acid and sodium chloride, using the same method and type of apparatus which they describe, excepting for the substitution of a Leeds & Northrup potentiometer for

¹ *J. Am. Leather Chem. Assoc.*, 12, 445 (1917).

² *ibid.*

the Wolff bridge. The temperature, which was not controlled, varied between 18 and 22°. Our results for N , $0.1 N$, and $0.025 N$ sulfuric acid, together with those of Thomas and Baldwin for $0.0005 N$ acid, are shown in Table I and Fig. 1.

TABLE I.—EFFECT OF NaCl UPON HYDROGEN-ION CONCENTRATION OF SOLUTIONS OF SULFURIC ACID.

Moles NaCl per liter.	Log $[H^+]$ of $N-H_2SO_4$	Log $[H^+]$ of $0.1 N-H_2SO_4$	Log $[H^+]$ of $0.025 N-H_2SO_4$	Log $[H^+]$ of $0.0005 N-H_2SO_4$
0.000	-0.36	-1.22	-1.72	-3.50
0.428	-1.13	-1.62
0.856	-1.04	-1.56
1.000	-0.15	-3.29
1.784	-0.96	-1.45
1.712	-0.87	-1.37
2.000	+0.03	-3.10
2.140	-0.77	-1.27
3.000	+0.24	-2.92
3.210	-0.55	-1.05
4.000	+0.45	-2.71
Value of b	0.20	0.21	0.21	0.20

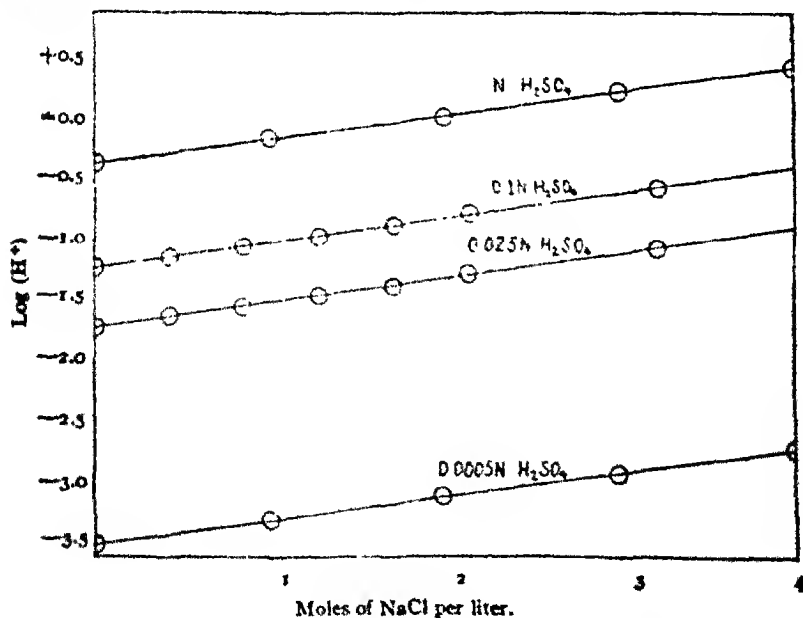


Fig. 1.

Apparently the curves are not only straight lines, but all 4 have the same slope, the average value for b being 0.205. The large percentage increase in hydrogen ion concentration upon the addition of 4 moles

per liter of sodium chloride and the fact that it is practically the same, about 560%, for widely different strengths of acid, suggest that the effect must be due to some action of the salt upon the solvent, such as hydration. It is of course apparent that any increase in concentration of acid caused by hydration of the salt will result in a lesser percentage ionization of the acid, but at least 2 factors, other than hydration of the salt, will tend to cause an increase in hydrogen ion concentration, and these are the hydration of the acid itself and the fact that with increasing salt concentration there will be less total water, free and combined, per liter of solution. If these opposing tendencies exactly balance each other, that is, if they operate so that the percentage increase in hydrogen ion concentration found is equal to the percentage increase in concentration of total acid, then it is an easy matter to calculate the degree of hydration of the salt for any concentration. The fact that we get the same slope for all 4 curves seems to show that here the opposing tendencies are nearly balanced. Nevertheless, this may not prove true for other cases, so the safer plan would be to select acid solution so dilute as to make these opposing tendencies of negligible magnitude. It would appear, however, in the case of sulfuric acid, that $b = 0.205$ for sodium chloride in all concentrations of acid less than normal. Let us, therefore, calculate the degree of hydration of salt in a solution of acid so dilute that we may neglect the hydration of the acid and its partial volume and consider it totally ionized.

From Equation 1 $\log ([H^+]/a) = bm$. But $[H^+]/a$ is the factor by which the acid concentration has been multiplied by adding m moles per liter of salt. Let w represent the total number of moles of water, free or combined with salt, in one liter of solution containing m moles of salt. The moles of free water then equal w , $[H^+]$ and the moles of water combined with one mole of salt equal $(w/m) \times (1 - a/[H^+])$. Calling this latter value h , we have

$$h = w (1 - 10^{-bm}) m. \quad (2)$$

Substituting 0.205 for b in Equation 2, we have calculated the degree of hydration of sodium chloride for several concentrations. (See Table II.)

TABLE II.—CALCULATED VALUES FOR DEGREE OF HYDRATION OF NaCl AT DIFFERENT CONCENTRATIONS.

Moles NaCl per liter. (m).	Total moles water per liter. (w)	Molecules water combined with one molecule of NaCl (h).
4.0	51.1	10.9
3.0	52.3	13.2
2.0	53.5	16.3
1.0	54.6	20.5
0.1	55.4	23.5
0.01	55.5	26.1
0.001	55.5	26.2
0.000	55.5	26.2

The striking agreement between our value 26.2 for infinite dilution and Smith's¹ calculated value of 26.5 by quite another method confirms the idea that hydration of the salt is responsible for the increase in hydrogen-ion concentration noted.

When it is required to calculate the degree of hydration only for infinite dilution, Equation 2 may be greatly simplified, since

$$\lim_{m \rightarrow 0} h = w(10^{bm} - 1)/m = 2.30wb = 128b. \quad (3)$$

Conversely, given the degree of hydration at infinite dilution, one may simply divide by 128 to get b and substitute in Equation 2 to calculate hydration values for any finite concentrations, provided of course the degree of hydration follows the rule expressed by Equation 2.

For the sake of comparison we made a set of determinations with N sulfuric acid and potassium chloride, the results of which are given in Table III. Since $b = 0.14$, the degree of hydration at infinite dilution would be 128 times as great, or 18, which is not far from Smith's value of 19.2.

TABLE III EFFECT OF KCl UPON HYDROGEN ION CONCENTRATION OF N SULFURIC ACID

Moles KCl per liter	Log [H ⁺]
0.0	-0.36
1.0	-0.21
2.0	-0.09
3.0	+0.05
<hr/>	
Value of b	0.14

Thomas and Baldwin's results with hydrochloric acid show greater slopes for the alkali chlorides in 0.004 N than in 0.1 N acid. For each salt the value of b is less in the stronger solution by about 15% of its value in the weaker one. Since complications introduced by the acid would naturally be less noticeable in more dilute solutions, the values of b in the weaker acid may be taken as more nearly representing the true index of hydration of the salts. Values for 128 b in 0.004 N hydrochloric acid follow: potassium chloride, 15; ammonium chloride, 15; sodium chloride, 26; lithium chloride, 35, and barium chloride, 50. Smith's corresponding values are potassium chloride, 19.2; ammonium chloride, 20.3; sodium chloride, 26.5; and lithium chloride, 33.6. Considering the limits of accuracy of the method as employed, the fact that temperature was not controlled, and that hydration of the acid and the repression of its ionization were ignored, the similarity between these 2 sets of results seems more than a coincidence. In fact, the writer believes it strongly confirms, for chlorides, the earlier view that the neutral salt effect is due to hydra-

¹ THIS JOURNAL, 37, 722 (1915)

tion and also the suggestion¹ that the Hofmeister series of the ions owes its nearly fixed order to the fact that the degree of hydration of the ions runs in the same order.

The peculiar behavior of the sulfates of sodium and ammonium in lowering the hydrogen-ion concentration of acid solutions, when one might have expected them to raise it very materially, may after all be found to be due to the same forces as bring about hydration. Their action can hardly be simply that of repressing the ionization of the acid because of their effect upon chrome liquors, whose resistance to precipitation by alkalis they increase very much more than chlorides do, and this in view of the fact that in some cases they lower the hydrogen-ion concentration to a point at which precipitation of basic chromic salts might be expected without any addition of alkali. The tendency of sulfates to form addition compounds may eventually afford an explanation.

The nearly quantitative agreement between hydration values of the alkali chlorides at infinite dilution given by Smith and those calculated in this paper from hydrogen-ion measurements seems to warrant a much more extensive pursuit of the subject and especially of the use of the electrometric method for studying hydration and its effect upon concentrated solutions.

MILWAUKEE, WIS.

THE ACTIVATION OF HYDROGEN PEROXIDE BY LIGHT.

By HARRY A. CURTIS

Received January 21, 1920

Introduction.

In studying the photolysis of hydrogen peroxide at the University of Wisconsin several years ago, it was noted by the writer that the oxidizing power of dilute hydrogen peroxide is increased when the solution is exposed to the light from a mercury vapor quartz lamp. Later this activation of hydrogen peroxide was investigated further by the writer and one of his students, Mr. Benjamin D. Cornell, at the University of Colorado. The work was interrupted by the war before it had been carried to a logical conclusion, but it appears worth while to record the results obtained.

Method.

By working with a considerable number of dyes, a few were found which, under the conditions of the experiment, were not bleached to any great extent by either light alone or the peroxide alone, but which were bleached colorless after a few hours exposure to light in the presence of

¹ *J. Am. Leather Chem. Assoc.*, 13, 179 (1918).

hydrogen peroxide. Aniline green and fuchsine were finally chosen as suitable for the experiments in hand. Stock solutions of these dyes were made up with distilled water. The hydrogen peroxide solution was made by diluting 30% "Perhydrol" with distilled water to a concentration of about 3%, and was kept in paraffin-lined flasks. Reaction mixtures were made by diluting the stock dye solution with an equal volume of distilled water or with an equal volume of the 3% hydrogen peroxide. When the reaction mixture was to be exposed to light, it was placed in a quartz flask mounted along side the lamp. Water from a large thermostat was circulated over the flask and the reaction mixture was gently stirred during illumination¹. The rate of bleaching of the dye was followed by means of a Hellige-Leitz colorimeter. For dilute dye solutions, such as used, the readings of the instrument are inversely proportional to the amount of dye in solution.

Experimental Results.

A.—The effect of the light in hastening the bleaching of the dye (aniline green) in the presence of hydrogen peroxide is shown in the following table, and is represented graphically in Fig. 1.

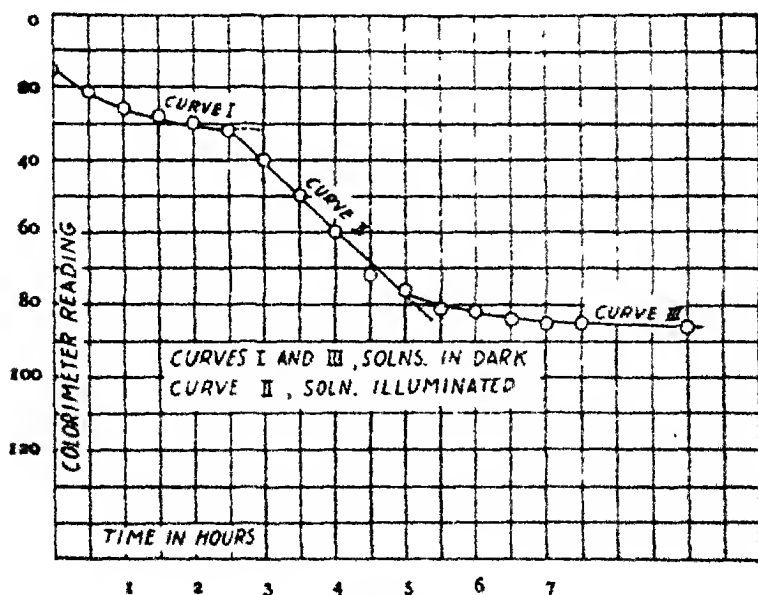


Fig. 1.

¹ For a diagram of this apparatus see Mathews and Curtis, *J. Phys. Chem.*, 18, 321 (1914).

HARRY A. CURTIS.

TABLE I.—EFFECT OF LIGHT ON BLEACHING.

Time. Reaction mixture in the dark a.m.	Colorimetric readings	Time. Light cut off at 12.30 p.m.	Colorimetric readings
8.00	15	1.00	76
8.30	21	1.30	81
9.00	26	2.00	82
9.30	28	2.30	84
10.00	30	3.00	85
10.30	32	3.30	85
		3.00	86
Reaction mixture exposed to light at 10.30 a.m.			
11	40		
11.30	50		
12.00	60		
p.m.			
12.30	72		

B.—Three reaction mixtures were made, one of them containing the dye solution diluted with an equal volume of distilled water, the other 2 containing both the dye and the peroxide. The dye solution and one of the dye-peroxide solutions were exposed to the light, the other dye-peroxide solution being kept in the dark. Results tabulated below are shown graphically in Fig. 2

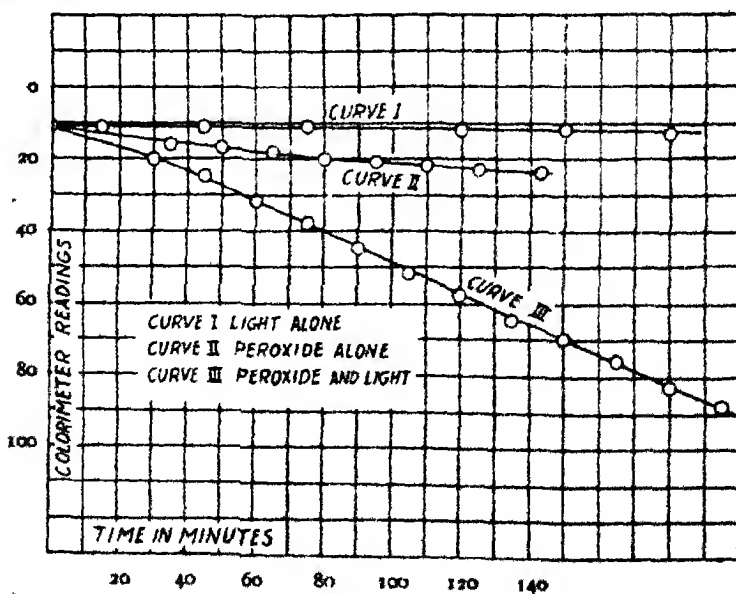


Fig 2.

TABLE II.—EFFECT OF PEROXIDE AND LIGHT ON BLEACHING

Action of light alone		Action of peroxide alone		Action of peroxide and light	
Time, minutes	Reading	Time, minutes	Reading	Time, minutes	Reading
0	11	0	11	0	11
15	11	35	16	30	20
45	11	50	17	45	25
75	11	65	18	60	32
120	12	80	20	75	38
150	12	95	21	90	45
180	13	110	22	105	52
		125	23	120	58
		143	24	135	65
				150	70
				165	76
				180	83
				195	88

C.—Since ozone is produced by exposing oxygen to light of short wave lengths it might be thought that the effect when both light and peroxide were used resulted from an ozonizing of the oxygen liberated from the peroxide. Such is apparently not the case, for if oxygen be bubbled in a fine stream through the dye solution under exposure to light the following results are obtained.

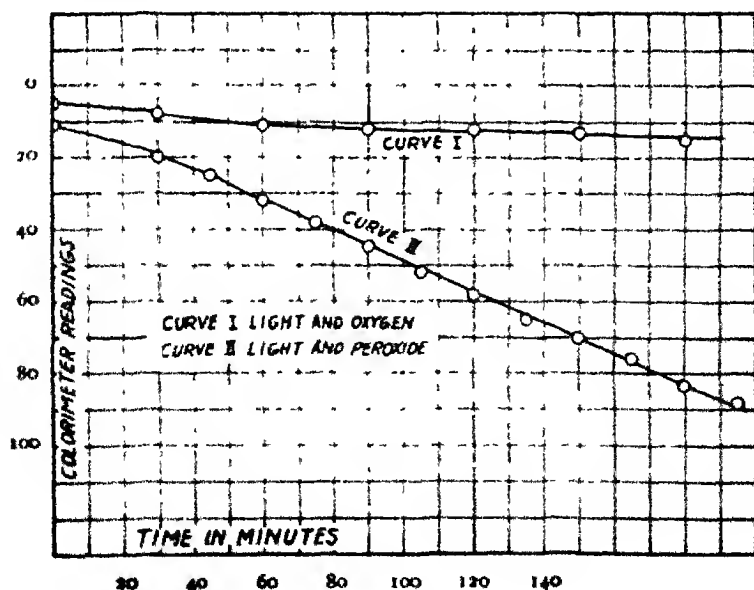


Fig. 3.

TABLE III.—EFFECT OF OZONE AND LIGHT ON BLEACHING.

Time, minutes.	Reading.	Time, minutes	Reading
0	5	120	12
30	8	150	13
60	11	180	15
90	12		

In Fig. 3 the above data are plotted together with those for the combined light and peroxide from the earlier table.

Summary.

It has been shown that the oxidizing power of hydrogen peroxide, as manifested in the bleaching of dyes, is increased by exposing the reaction mixture to light of short wave lengths.

This effect cannot be duplicated by substituting oxygen for hydrogen peroxide in the reaction mixture, indicating that the result is not due to formation of ozone.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF GRINNELL COLLEGE]

FURTHER WORK ON POTASSIUM HYDROGEN PHTHALATE AS A STANDARD IN VOLUMETRIC ANALYSIS.

By W. S. HENDRIXSON

Received January 28, 1920

Several years ago the writer showed that potassium hydrogen phthalate and sodium hydrogen phthalate may be used with advantage as standard in volumetric analysis.¹ They can be prepared easily in a state of great purity, they have large molecular weights, 204.14 and 188.04, respectively, and only one hydrogen ion. The potassium salt has the great advantage of absence of water of crystallization. So little work has been done on these salts and so little is known of their properties that it seemed desirable to study further the potassium salt, which is to be preferred as a standard. The objects were: (1) to determine the practicability of the preparation and use of the salt as a standard, by others; (2) to determine the necessary degree of purification for ordinary purposes, and the yield on the basis of the phthalic anhydride used; (3) to determine the hygroscopic character of the salt and the means necessary to dry it.

The laboratory work on potassium hydrogen phthalate here described was done by Mr. Sereno Norton, then a senior in Grinnell College, now a chemist with the Hercules Powder Company.

The potassium hydrogen phthalate was prepared by the method described in the paper already cited. Several preparations were made and titrated. There is one chance of error in its preparation, which might easily be made by comparatively inexperienced hands, and which should

¹ THIS JOURNAL, 37, 2352 (1915).

be mentioned. Phthalic anhydride is very sparingly soluble even in hot water. If not enough potassium carbonate is used in the neutralization a portion of the anhydride will be left undissolved, and may easily be overlooked, since the sparingly soluble acid phthalate is likely to form a layer of crystals over the hot solution. Since the neutral potassium phthalate is extremely soluble even in cold water there is no danger of its contaminating the acid salt. Therefore, a slight excess of the carbonate should be used, and the hot solution should be filtered in the first instance.

A large volume of standard hydrochloric acid was made by the admirable and accurate method of Hulett and Bonner,¹ so as to contain 0.003647 g. of hydrogen chloride to one cc. This acid was titrated through the medium of sodium hydroxide against benzoic acid specially prepared for such purposes by the Bureau of Standards, which gave 0.003648 g. to one cc. This concentration was confirmed by means of silver. The solution of sodium hydroxide, free from carbonate, was prepared as described in the first paper, and was used as the intermediary between the acid phthalate and the hydrochloric acid. The indicator was phenolphthalein, and as pointed out in the former paper its error in marking the end-point was cancelled by the method of titration. The same weight burets and calibrated flasks described in the former paper were used in this work.

Titration were made of samples of potassium hydrogen phthalate which had been 3, 4 and 5 times recrystallized from hot water. The objects were to determine the number of crystallizations necessary to secure a sufficiently pure product, and to determine the constancy of the acid salt as an individual compound. It is well known that some so-called acid salts do not show constancy in composition on being repeatedly crystallized. The results are given in the following table in which "three," "four" and "five" indicate the number of recrystallizations, and below each are the values given for the standard hydrochloric acid, assuming the formula value of the acid phthalate.

Evaluation of 0.1 N HCl with $\text{HKC}_8\text{H}_4\text{O}_6$ through Standard NaOH.			
Numbers of titrations.	Three	Four.	Five.
(1)	0 0036489	0 0036470	0 0036519
(2)	0 0036473	0 0036475	0 0036455
(3)	0 0036484	0 0036449	0 0036448
(4)	0 0036480	0 0036450	0 0036410
(5)	0 0036471
(6)	0 0036475
(7)	0 0036478
(8)	0 0036463
(9)	0 0036463
(10)	0 0036455
Averages:	0 003647	0 003646	0 003646

¹ THIS JOURNAL, 31, 390 (1909).

The results seem to show that there is nothing gained by more than 3 recrystallizations. Other results not here given seemed to show that for ordinary purposes even 2 recrystallizations, that is, 3 crystallizations in all would suffice. There seems to be no reason to doubt the constancy of the composition of the acid salt.

Working with no special precautions to secure a large yield our results show that about 50% of the theoretical yield of the acid salt may be obtained after 4 recrystallizations. Though expensive in war time, thanks to recent improvements in its preparation phthalic anhydride of great purity is again becoming abundant and cheap. Potassium carbonate of great purity is not difficult to obtain, and therefore, potassium hydrogen phthalate is one of the standards most easily and cheaply obtained.

We next directed our attention to the hygroscopic character of potassium hydrogen phthalate. It is very desirable that a substance used as a standard should have a low hygroscopicity. To test this character we carried out 2 sets of experiments. The first consisted in heating the air-dried salt in an electric oven at different temperatures, determining the losses in weight and the effect upon the titration value of the salt. The second consisted in exposing the substance thus dried in air of known moisture content, and determining the amount of moisture taken up from the air,

In carrying out the first set of experiments about 20 g. of the salt was heated in the electric oven in a platinum dish. At the end of each period the loss was determined and a portion of the substance was taken out without loss and titrated. The losses and titrations should thus form checks on each other. There were 11 such titrations, but since only 4 different temperatures were used, the results at the same temperature are combined in the following table:

Wt. of salt	Time	Temp	Loss	Value of HCl
21.5940	4 hrs.	110	0.0006	0.0036471
20.4956	2 hrs.	120	0.0024	0.0036469
16.0100	8 hrs.	130	0.0034	0.0036490
11.6910	8 hrs.	150	0.0006	0.0036473

It is remarkable that the hygroscopic moisture which should have been eliminated at 110° is so small, one part in about 36,000. Doubtless a part of the loss at higher temperatures is to be ascribed to changing atmospheric conditions, possibly to undetected losses in taking out portions for analysis. Granting that all the apparent loss was due to water, its total, calculated on the basis of the original weight of salt taken, is 0.0088 g. or one part in about 2500, which is outside the limit of accuracy of titration in ordinary work.

The hygroscopic character was further studied by exposing the salt re-

maining, and dried as above, in an atmosphere of known moisture content. The platinum dish and salt were placed in a desiccator which contained sulfuric acid so diluted as to give to the air above it a humidity of 70%, which is not likely to be exceeded in the air of a laboratory. From time to time during 47 days the dish and contents were weighed. The gain or loss as compared with the previous weight never exceeded 0.002 g. and at the end of the period, summing up the gains and losses, there was found a loss of 0.0001 g.

These 2 sets of experiments seem to show that the hygroscopicity of potassium hydrogen phthalate is practically nothing, and in using it and weighing it attention need be directed only to the containing vessel. By use of an open platinum crucible in weighing it, it is believed that this source of error has been almost completely avoided.

In the preparation of potassium hydrogen phthalate it is desirable to know its solubility in hot and cold water, and this was determined at 25 and 35 degrees and at the boiling point of its saturated solution. At the lower temperatures the method used was one devised by the writer.¹ For the solubility at the boiling point the method of Pawlewski² was used.

Solubility of Potassium Hydrogen Phthalate in Water

Temp.	Wt. solution	Wt. acid phthalate	% m sol
At 25 degrees	21.025	2.1531	10.23
	21.028	2.1553	10.25
At 35 degrees .	21.198	2.6859	12.67
At boiling point	9.18	3.3158	36.12

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE EFFECT OF SOLVENT ON THE ULTRA VIOLET ABSORPTION SPECTRUM OF A PURE SUBSTANCE.

By F. O. RICE.

Received January 28, 1920

In a previous paper¹ some quantitative measurements were described showing the absorption of acetone and its homologues in the pure liquid condition. A large quartz spectrograph fitted with a spectrophotometric arrangement was used and by this means the extinction coefficient, ϵ , is given by $\epsilon = 1/d (\log I_0/I)$, where I_0 is the intensity of the incident light, I the intensity of the emergent light, and d the thickness of the absorbing layer. ϵ may, therefore, be defined as the reciprocal of that thickness of medium which reduces the intensity of the light to $1/10$ of its original value.

* If c be the normality of the ketone (sp. gr. \times (1000/mol. wt.)) the molecular extinction is given by $M = \epsilon/c$.

¹ *Proc. Iowa Acad. Sci.*, 23, 31 (1916).

² *Ber.*, 32, 1040 (1899).

³ *Proc. Roy. Soc. (London)*, 97A, 76 (1914).

The molecular extinction curves are obtained by plotting the values of M on the ordinate against the corresponding wave lengths on the abscissa. Known thicknesses of the various ketones were obtained by making up a number of cells consisting of 2 plain parallel quartz plates cemented together with a wire ring of known diameter. The error in measuring the center of the absorption band was in most cases about 3 Ångström units, but in certain cases in the present investigation where the solvent had comparatively high absorptive power the error may be as great as 6 units. The error in the value of the molecular extinction is in general about 6%.

The ketones as ordinarily purchased contain small quantities of unsaturated substances which cannot be entirely removed by fractional distillation. This can be shown by treating a few drops of a carefully distilled ketone with dil. aqueous potassium permanganate, when immediate oxidation takes place. These impurities must be removed because their absorptive power may be up to 500 times that of the ketone, and the presence of only $1/2\%$ may completely mask the absorption of the ketone itself. This fact was not realized in previous investigations, and most of the published work is quite valueless, due to the use of impure specimens of ketones. Throughout the present work the greatest care was taken to ensure the purity of the ketones, and the methods used have been described in previous papers by the author.

When the pure liquid ketones were examined certain striking regularities were observed in their absorptive action towards light. It can be stated that all saturated aliphatic ketones are practically diactinic between 7,000 Å. U. and 3,200 Å. U. Between 3,200 Å. U. and 2,300 Å. U. there is an absorption band and from 2,300 to 2,100 Å. U. all of the ketones again become diactinic. There are no exceptions to the rule, such ketones as hexamethyl acetone and methylnonyl ketone behaving precisely like acetone in this respect. The wave length between 3,200 and 2,300 Å. U. at which maximum absorption occurs varies with the ketone and depends on the number of hydrogen atoms in the α or β position which are substituted by alkyl radicals. Substitution of other hydrogens has no effect on the absorption so that all ketones of the general formula $\text{CH}_3\text{COCH}_2\text{CH}_2\text{R}$ have maximum absorption at 2,790 Å. U.

This effect of substituting α or β hydrogens is in general to move the absorption maximum towards the red end of the spectrum; thus the absorption maxima for acetone, pinacolone, $(\text{CH}_3)_2\text{CCOCH}_3$, hexamethyl acetone, $(\text{CH}_3)_2\text{COC}(\text{CH}_3)_2$ are, respectively, 2747, 2850, 2950 Å. U., intermediate effects being obtained with other ketones.

With regard to the value of M , the molecular extinction at the point of maximum absorption, all of the ketones with the exception of acetone and methylethyl ketone have the same value, namely 21.2. The values for these 2 ketones are 17.1 and 19.4, respectively, and this deviation is

probably due to association. Assuming that the absorption power of the associated molecules is inversely proportional to the number of simple molecules in the complex, the association factor of these 2 ketones can be calculated.

The foregoing is a brief summary of the author's work on the absorptive power of the pure liquid ketones. In the present paper the effect of dissolving the ketones in various solvents is examined.

The first question which came up was whether or not it was necessary to submit the solvent used to the same rigorous purification as was necessary with the pure ketones. In the spectrophotometer the actual mechanical absorption of the solvent was corrected for by placing in the lower beam of light the amount of solvent used, the solution being in the path of the upper beam. There remains, however, the possibility of some further effect between the dissolved ketone and the impurities, as for example, in cases of catalysis where an impurity may have an effect out of all proportion to its concentration. To test this point some acetone was freshly prepared from the bisulfite compound, dried with the greatest care, and placed in a specially dried cell and its absorption at once measured.

Acetone, which had been exposed to air and a specimen to which 1% of water had been added, were also examined, but in all 3 cases the center of the absorption band was at $\lambda = 2747$. That the presence of small quantities of water has a negligible effect is also shown by experiments with acetone dissolved in various solvents. An 0.8 molar solution in ordinary absolute alcohol (99.6%) showed the center of absorption at $\lambda = 2725$. Absolutely dry alcohol was prepared by the method of Young and Fortey,¹ and the center of the band when acetone was dissolved in this solvent was also at $\lambda = 2725$, so that the small quantity of water present in ordinary absolute alcohol makes no difference.

Experiments with dry chloroform and chloroform saturated with water (about 0.3%) gave the same result as did chloroform containing a small quantity of piperidine. Generally it may be stated that in no case did a small quantity of a second solvent (up to 1 or 2%) cause any appreciable movement of the centre of the absorption band with acetone or any of the aliphatic ketones. This result is important because it shows that there is no need to purify a solvent rigorously, small traces of impurities having no appreciable effect on the absorption band. It must be noted, however, that this holds good only when the absorption of the impurity is corrected for by placing an equivalent quantity of the solvent in the path of the lower beam of light. The ketone studied must also be optically pure, for if it contains any impurity, the absorption of the latter would be superimposed on that of the ketone itself and would thus lead to error.

¹ *J. Chem. Soc.*, 81, 717 (1902).

It was soon found that any effect produced in the absorptive power of acetone by a solvent was produced also on any of the higher ketones, but in a less degree. (See Table I) It will be noticed that hexamethyl acetone gives no movement of the absorption band when dissolved in alcohol, nor does it give any movement when dissolved in water-alcohol mixtures. This accords well with the fact that this ketone does not form an oxime, hydrazone or semicarbazone, due probably to the steric effect of the adjacent methyl groups which also apparently prevent any hydrating of the carbonyl group by the solvent. In the case of solvents, such as hexane and carbon tetrachloride, where there is a movement of the band towards the red, hexamethyl acetone behaves normally.

TABLE I.—EFFECT OF SOLVENT ON ABSORPTIVE POWER OF KETONES.

Ketone	Pure liquid λ	Aqueous			Ethyl alcohol			Heptane			Chloroform		
		M	λ	Shift	M	λ	Shift	M	λ	Shift	M	λ	Shift
Acetone	2747	18.8	2645	—102	18.0	2725	—22	17.1	2785	+38	17.1	2745	0
Methylethyl	2770	20.9	2665	—95	19.8	2750	—20	19.4	2799	+29	19.4	2770	0
Methyl-													
propyl	2790	21.2	2695	—95	21.2	2770	—20	21.2					
Methylbutyl	2790	21.2	2700	—90	21.2	2770	—20						
Methyl													
isopropyl	2820	21.2	2735	—35	21.2	2800	—20	21.2	2845	+25			
Methyl													
isobutyl	2810	21.2	2725	—85									
Methyl													
tert. butyl	2850	21.2	2760	—90				21.2	2870	+20	21.2	2850	0
Diethyl	2780	21.2	2690	—85									
Ethylpropyl	2800	21.2	2720	—80	21.2	2790	—20	21.2	2815	+15	21.2	2800	0
Hexamethyl	2950				21.2	2950	0	21.2	2965	+18	21.2	2950	0

M = molecular extinction of the ketone at the wave length of maximum absorption λ . The concentration of the ketones was about 0.1 molar.

The extinction coefficient ϵ of a ketone dissolved in a solvent will vary with the concentration of the solution, but if the molecular extinction is calculated by dividing ϵ by the concentration of the ketone in gram moles per liter, then according to Beer's law¹ the value of the molecular extinction will not be affected by solvents or dilution. There has been much controversy regarding the reasons why some substances do not obey this law, which, of course, presupposes that the molecules of the ketones are not affected by the solvents.

In this investigation it was found that deviations from Beer's law occurred only with acetone and methylethyl ketone, and the molecular extinctions of all other ketones are constant (21.2) whether the ketone is in the pure state or in solution.

The value of M for pure liquid acetone is 17.1, and this value is not changed by solution in hexane, chloroform, or other non-dissociating sol-

¹ *Pogg. Ann.*, 86, 78 (1852).

vents. Solutions of acetone of about 0.1 molar concentration in ethyl alcohol and water give values of M equal to 18.6 and 18.8, respectively.

TABLE II.—CHANGE IN THE POSITION OF THE ABSORPTION MAXIMUM WITH GRADUAL ADDITION OF WATER.

Normality.	L .	λ	$\lambda_1 - \lambda$.
13.8	0.07	2747	0
10.9	0.09	2716	31
8.4	0.12	2687	70
5.7	0.17	2662	85
2.4	0.42	2659	88
1.0	1.0	2657	90
0.24	4.2	2651	96
0.12	8.3	2645	102
0.04	25.0	2640	107
0		2637	110

L = liters of solution containing one g. mol. of acetone.

λ = wave length of maximum absorption

λ_1 = wave length of maximum absorption for pure acetone.

It seems very probable, therefore, that the deviation of acetone and methylethyl ketone is due to part association of the molecules and partial breaking down of this association by an ionizing solvent such as water. The value of the molecular extinction for aqueous acetone is nearer to the normal value 21.2. In the case of the aliphatic ketones there is no deviation from Beer's law in passing from the pure state to solution in many different solvents except in the cases of acetone and methylethyl

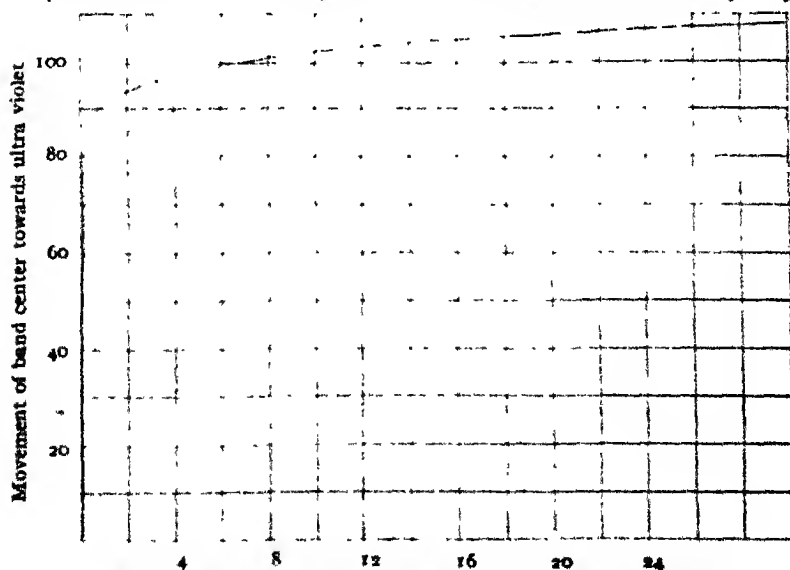


Fig. 1.—Liters of aqueous solution containing 1 g. mol. of acetone.

ketone, when deviations are to be ascribed to disruption of associated molecules by an ionizing solvent. Table II shows the change in the position of the absorption maximum with gradual addition of a solvent (water) to pure acetone, the last line of the table being obtained by extrapolation. The water causes the center of the absorption band to move towards the ultra violet, the movement increasing with dilution up to wave length 2637, at which point (see Curve I) it becomes asymptotic.

Exactly analogous effects were observed when other solvents were gradually added to acetone, but owing to the much smaller shifts of the

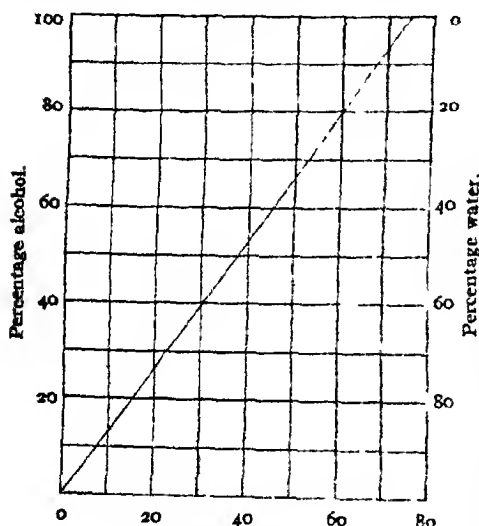


Fig. 2.

band center the experimental error was too great to allow accurate curves to be drawn.

Fig. 2 was obtained by starting with an 0.8 M solution of acetone in water and gradually displacing the water by alcohol, the strength of acetone being kept constant. In this case the effect is directly proportional to the quantity of alcohol added. This was found to hold generally for mixtures of 2 solvents, and enables us to state the general rule that if an absorbing substance is dis-

solved in one solvent and if this solvent is gradually displaced by another solvent (the strength of the solute being kept constant) the movement of the absorption band is directly proportional to the percentage of the second solvent present.

Let A and B be the two solvents; and let λ_A = the point of maximum absorption in A; and λ_B = the point of maximum absorption in B; and let $x\%$ of B be present in the mixed solvent, then the maximum absorption in the mixed solution will be given by

$$\lambda_1 = \lambda_A + x/100 (\lambda_A - \lambda_B).$$

It will be seen that a small quantity of impurity (where $x = 1$ or 2%) in a solvent will have a negligible effect, providing its mechanical absorption is corrected for in the usual way.

The variation in the position of the absorption maximum with the

nature of solvent, was first studied by Kundt,¹ who stated that with increasing refractivity of solvent the absorption band moved nearer the red. As a rough generalization (see Table III) Kundt's rule undoubtedly appears to hold good for in the case of these solvents with higher refractivity the band is generally nearer the red end of the spectrum. There are, however, several indications that it is not a hard and fast rule as, for example, in Table III, methyl acetate, which should give a shift similar to hexane, does not affect the position of the band.

TABLE III—KUNDT'S RULE.

Solvent	Mol. refractivity	Shift.
Hexane .	29.7	38
Carbon tetrachloride	26.4	43
Methyl acetate	29.36	0
Ether	22.31	27
Chloroform . .	21.31	0
Propyl alcohol	17.4	-11
Acetic acid .	12.9	-47
Formamide	8.5	-42
Methyl alcohol	8.13	-44

In the column headed "shift" is given the difference between the centre of the absorption band of pure acetone and of acetone dissolved in the various solvents.

With regard to the dielectric constants a similar effect may be observed, for in the cases of those solvents with low values of the dielectric constant the centre of the band is nearer the red end of the spectrum. But as before, this is only a rough generalization.

An interesting study was made of the effect of using an homologous series of compounds as solvents, the case of the aliphatic alcohols being shown in Table IV, acetone of about 0.08 *M* being used as solute.

TABLE IV—EFFECT OF HOMOLOGOUS SERIES, WITH ACETONE AS SOLVENT.

Solvent.	Center of band	Shift.
Methyl alcohol	2720	-27
Ethyl	2730	-17
Propyl	2737	-10
Isopropyl	2737	-10
Butyl . .	2736	-11
Isobutyl	2734	-13
Tert butyl	2735	-12
Iso amyl .	2736	-11
Sec. amyl	2740	-7
Octyl	2738	-9

- * It will be seen that with the exception of methyl and ethyl alcohols which are abnormal the alcohols give a constant shift of 11 units. This shift is similar to the series constant in other physical measurements, such as refractivity and magnetic rotation. The saturated hydrocarbons also show a series constant, those examined being pentane, hexane, heptane,

¹ *Ann. Phys.*, 4, 34 (1878).

octane, decane, and cyclohexane, and giving a constant shift of 38 units towards the red. The chlorine derivatives of the paraffins examined were chloroform, dichloro-ethane, trichloro-ethane and chloropropane, all of which gave no movement of the band center. The series of fatty esters also gave no shift. The ether series (only one member examined) gave a shift of +27 units.

These results are tabulated in Table V, acetone again being used as solvent.

TABLE V—COMPARISON OF SERIES OF HOMOLOGUES, USING ACETONE AS SOLVENT

Solvent	Number examined	Average center	Series constant
Hydrocarbons	6	2785	38
Chlorohydrocarbons	4	2747	0
Alcohols	10	2736	-11
Acids	2	2724	-23
Esters	3	2747	0
Ethers	1	2774	27

A summary of the effect of solvents, on the absorption by acetone, is given in Table VI and it will be seen that solvents fall into 2 main classes, namely those which move the band center toward the ultra violet and those which do not affect it or which move it towards the red.

TABLE VI—EFFECT OF SOLVENTS ON THE ABSORPTION BY ACETONE

Solvent	Normality	Mol extinction	Center	Shift
Water	0.1	18.8	2745	-102
Methyl alcohol	0.1	18.2	2703	-44
Ethyl alcohol	0.1	18.6	2720	-27
Higher alcohols	4.0	17.1	2736	-11
Acetic acid	4.0	17.8	2700	-47
Propionic acid	4.0	17.1	2724	-23
Phosphorus oxychloride	4.0		2718	-29
Formamide	4.0	18.8	2755	-45
Hydrocarbons (6)	4.0	17.1	2785	+38
Chlorocarbon, (4)	4.0	17.1	2747	0
Chlorocarbons	0.1	11.1	2745	0
Carbon tetrachloride	4.0	17.1	2789	+42
Ethyl ether	4.0	17.1	2774	+27
Methyl acetate	0.1	17.1	2747	0
Ethyl acetate	0.1	17.1	2747	0
Ethyl propionate	0.1	17.1	2747	0
Propyl acetate	0.1	17.1	2747	0

The difference between the two sets of solvents seems to be connected with their physico-chemical properties, especially their ionizing powers. The replacement of hydrogen atoms which either ionize themselves or confer ionizing properties on the solvent, causes the band of acetone to be displaced towards the red end of the spectrum.

This may be illustrated by the 3 compounds, water, ethyl alcohol, and ether. The very highly ionizing compound water, the slightly ionizing

compound ethyl alcohol, and the non-ionizing compound ethyl ether, shift the band of acetone by -102 , -22 and $+27$ units, respectively. Another example of this is given by the ionizing compound acetic acid, which displaces the acetone band 47 units towards the ultra violet, whereas the replacement of the hydrogen atom to give ethyl acetate entirely neutralized this effect, no shift being observed when acetone is dissolved in the ester.

Summary.

1. All of the aliphatic ketones except acetone and methylethyl ketone follow Beer's law, *i. e.*, the molecular extinction is independent of the concentration, and solvent.

With acetone and methylethyl ketone there are deviations when ionizing solvents are used, due to partial disruption of the associated molecules.

2. Kundt's Rule, which states that with increasing refractivity of solvent the band moves towards the red, holds good if regarded as a rough generalization.

3. When a pure substance is dissolved in an ionizing type of solvent the absorption center moves toward the ultra violet; if a pure substance is dissolved in a neutral non-ionizing type of solvent the absorption center is unaffected or moves towards the red end of the spectrum. It is probable that this is a general rule which holds good for all classes of absorbing substances.

The whole of the experimental part of this work was carried out in the Spectroscopic Department of Liverpool University, England. The author desires to express his sincere thanks to Prof. E. C. Baly for permitting him to make such full use of the facilities available there for this work

NEW YORK, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE DETERMINATION OF POTASSIUM AS PERCHLORATE. II.

BY GREGORY P. BAXTER AND MATSUSUKE KOBAYASHI.

Received February 2, 1920

Not long ago¹ we reported the results of experiments upon the quantitative handling of potassium perchlorate with special reference to its solubility in various washing media. After presenting additional evidence of the fact, already known, that the salt is soluble to a marked degree in even very concentrated alcohol containing perchloric acid, we supported the proposal of Davis² of using as a washing liquid alcohol containing

¹ THIS JOURNAL, 39, 249 (1917).

² J. Agr. Sci., 5, 32 (1912).

perchloric acid and previously saturated with potassium perchlorate. A further suggestion of working at 0° was made, since the uncertainty is almost halved owing to the lesser solubility at this temperature. The experiments showed beyond question that the procedure is adequate to prevent loss of potassium through solution in the washing liquid. When sodium perchlorate was present, however, the potassium perchlorate recovered was always in excess of the quantity originally taken, almost in proportion to the sodium perchlorate present. Part of this excess was unquestionably due to mechanical inclusion of the sodium salt in the particles of potassium perchlorate during evaporation of the aqueous solution of the original salts to dryness, since re-solution of the precipitate and evaporation, after extraction and removal of the sodium perchlorate, reduced this excess to a small fraction of the value it otherwise would have had. At the time we imputed the residual excess to inclusion, and it still seems probable that inclusion is responsible for a large part of the excess.

It was later pointed out, however, by Gooch and Blake¹ that a saturated alcoholic solution of potassium perchlorate may be caused to deposit a large part of the salt by dissolving in it sodium perchlorate. Apparently this takes place much more readily when the solution is in contact with solid potassium perchlorate. We had considered this point and, finding that the addition of sodium perchlorate to the saturated alcoholic solution produced no visible precipitate, concluded that no difficulty was to be feared from this source. Since the appearance of the paper by Gooch and Blake we have tested the matter further, with results which are in accordance with theirs.

In our earlier experiments, however, the difficulty could not have exceeded a few tenths of a milligram, for the total quantity of dissolved potassium perchlorate in the washing liquid is less than 2 mg. per 100 cc. Since the volume of washing liquid used in the initial extraction of the sodium perchlorate was always 20 cc., it is hard to believe that the error from this source could exceed 0.4 mg. in any case. This is exactly the error found in experiments with moderate quantities of sodium salts, if the original precipitate was dissolved and re-formed to avoid inclusion, although the maximum error, in the presence of nearly enough sodium perchlorate to saturate the extraction liquid, was 4 times as large. It is likely that a part of this larger error was due to inclusion even during the second evaporation.

It is, therefore, necessary to modify the treatment of the precipitate insofar as the initial extraction of the sodium salt is concerned, although the subsequent rinsing of the potassium perchlorate is best carried out with a saturated alcoholic solution of the salt as previously advocated.

¹ *Am. J. Sci.*, 44, 381 (1917).

Since the uncertainties involved are of small magnitude, the materials with which the following experiments were performed were very carefully purified. *Potassium perchlorate* was twice recrystallized from water. Fairly pure *perchloric acid* was distilled under reduced pressure in an all-glass apparatus, and was preserved in a quartz flask. *Sodium perchlorate* was prepared from sodium chloride. The latter substance was several times precipitated from aqueous solution with hydrogen chloride, the first and last solutions being freed from insoluble matter by filtration through a platinum-sponge crucible. In order to change the chloride to perchlorate, a solution of the salt was evaporated to dryness with an excess of perchloric acid, and the residue was several times dissolved and the solution evaporated to dryness with small amounts of perchloric acid. After the salt had been dissolved and the solution filtered through platinum sponge, the solution was again evaporated to dryness and the residue dissolved in alcohol containing 0.1% of perchloric acid. Filtration followed and the processes of evaporation, solution in alcohol and filtration were repeated. The final alcoholic solution was evaporated to dryness, and the residue was dissolved in water to make a 10% solution from which suitable quantities could be measured out for the separate experiments. *Alcohol* was dehydrated over lime and redistilled.

The first experiments were directed to determine how completely potassium perchlorate is salted out by sodium perchlorate. Sodium perchlorate solution was evaporated to dryness in a platinum dish and the salt was dissolved at 0° in alcohol containing 0.1% of perchloric acid and saturated with potassium perchlorate. Such an alcoholic solution will, in the following pages be designated *washing liquid*, and is indicated in the tables of results with the letter W. After standing 20 minutes the solution was filtered through a weighed platinum-sponge crucible, and the dish and crucible were thoroughly rinsed with washing liquid. Then the crucible was dried upon an electric stove at about 200°. The gain in weight of the crucible, which represents the potassium perchlorate salted out, gradually increases from an almost negligible quantity (0.1 to 0.3 mg.) with moderate concentrations of sodium perchlorate, (0.25 g. in 20 cc. washing liquid), to very nearly all of the dissolved potassium perchlorate when the washing liquid is nearly saturated with sodium perchlorate (one g. in 20 cc.). The data obtained in these experiments are given in Table I, Expts. 1 to 7.

Apparently the salting out of potassium perchlorate from the washing liquid is not to be feared if the quantity of sodium perchlorate is no more than a few tenths of a gram, while it cannot exceed 0.4 mg. for each 20 cc. of washing liquid used in the initial extraction, since this is the total quantity of dissolved salt. After the first extract has been decanted, so little

sodium perchlorate remains that the second addition of washing liquid will not result in further salting out.

In order to show that the sodium perchlorate itself was not responsible for any appreciable part of the gain of the crucible, similar experiments were performed using alcohol containing perchloric acid but no potassium perchlorate. Such a solution is indicated in the tables by the letter A. The gain in weight of the crucible did not exceed 0.1 mg. in any case. (Expts. 8 to 13.)

In order to determine whether sodium perchlorate can be completely washed out of a precipitate of the potassium salt, in Expts. 14 to 18 the dry sodium perchlorate was dissolved at 0° in absolute alcohol containing 0.1% of perchloric acid, and was poured upon a weighed quantity of finely powdered potassium perchlorate in a platinum dish. After being stirred the solution was allowed to stand a few minutes and then was filtered through a platinum-sponge crucible. The residue was washed by decantation many times with small portions of chilled washing liquid, and was dried and weighed. It is unlikely that the gain in weight, which occurred in every case, is due to potassium perchlorate salted out of the washing liquid, for the greater portion of the sodium perchlorate had been eliminated before even the first portion of washing liquid was added. Furthermore, the gain in weight seems to be roughly proportional not only to the quantity of sodium perchlorate, but also to that of the potassium salt. It seems more probable, therefore, that this gain is due to adsorption of the sodium perchlorate by the precipitate. In practice such a difficulty need not be feared, however, since solution of the original precipitate and re-evaporation may be depended upon to eliminate such impurity.

This effect is apparently somewhat irregular. At any rate, in Expt. 19, which was identical with Expt. 15 except that the initial extraction was made with washing liquid instead of alcohol, the excess in weight of recovered material was no greater than in the latter experiment.

The foregoing experiments confirm Gooch and Blake's observation that if washing liquid is used in the initial extraction of the potassium perchlorate, when a considerable amount of sodium perchlorate is present appreciable amounts of potassium perchlorate may be salted out of the washing liquid. On the other hand, the error introduced in this way under no circumstances is likely to exceed one mg., since even at room temperature alcohol containing perchloric acid will dissolve no more than this weight of potassium perchlorate in a 20 cc. portion, while at 0° the possible error is limited to half this quantity. It should be noted that the higher figures given by Gooch and Blake refer to 50 cc. of alcohol at room temperature and containing no perchloric acid.

TABLE I

Expt	First extract Cc	Washings Cc	NaClO ₄ taken G	KClO ₄ taken G	KClO ₄ found G	Error G
1	W 20	W 50	0.25		0.0001	
2	W 20	W 50	0.25		0.0003	
3	W 20	W 50	0.5		0.0002	
4	W 20	W 50	0.5		0.0004	
5	W 40	W 50	1.0		0.0006	
6	W 40	W 50	2.0		0.0006	
7	W 40	W 50	2.0		0.0007	
8	A 20	W 50	0.5		0.0001	
9	A 20	W 50	0.5		0.0001	
10	A 20	W 50	1.0		0.0001	
11	A 20	W 50	1.0		0.0001	
12	A 40	W 50	2.0		0.0001	
13	A 40	W 50	2.0		0.0001	
14	A 20	W 95	0.25	1.0011	1.0015	+0.0004
15	A 20	W 100	1.0	0.3021	0.3024	+0.0003
16	A 20	W 100	1.0	0.1033	0.1014	+0.0001
17	A 20	W 110	1.0	1.0019	1.0030	+0.0011
18	A 20	W 105	1.9	1.0009	1.0016	+0.0007
19 ..	W 20	W 80	1.0	0.3010	0.3013	+0.0003

Next several experiments were performed to determine, under the conditions of our experiments, the magnitude of the loss of potassium perchlorate through solubility, if the alcohol is not previously saturated with this salt. A weighed quantity of potassium perchlorate was dissolved in water together with approximate quantities of sodium perchlorate, and the solution was evaporated to dryness with an excess of perchloric acid. The residue was extracted at 0° with alcohol containing 0.1% of perchloric acid, and was washed by decantation twice with small portions of a similar solution. In order to avoid inclusion of sodium salt, the precipitate was dissolved in water and the solution was again evaporated to dryness with a small quantity of perchloric acid. Extraction and washing with an alcoholic solution of perchloric acid followed, and the precipitate was collected and dried. In these experiments, Table II, Nos. 20 to 25, a negative error occurred in every case. Two similar experiments at room temperature, Nos. 26 and 27, showed somewhat larger losses. It is obvious that the apparent error from solubility will be less with larger amounts of sodium perchlorate, partly owing to the lessened solubility of the precipitate, partly owing to compensation by inclusion of the sodium salt by the precipitate, even when solution and re-formation of the precipitate during the washing occurs. With more dil. alcohol, also, the error will become larger.

TABLE II.

Expt.	First extract. Cc.	Washings. Cc.	NaClO ₄ taken. G.	KClO ₄ taken. G.	KClO ₄ found. G.	Error. G.
20.....	A 20	A 105	0.1	0.3007	0.2995	-0.0012
21.....	A 20	A 100	0.5	0.3007	0.3005	-0.0002
22.....	A 20	A 105	0.5	0.3011	0.3007	-0.0004
23.....	A 20	A 110	1.0	0.3004	0.3001	-0.0003
24.....	A 20	A 110	1.0	0.3007	0.2992	-0.0015
25.....	A 20	A 90	1.0	0.3007	0.3007	-0.0000
26.....	A 20	A 100	0.1	0.3005	0.2991	-0.0015
27.....	A 20	A 95	1.0	0.3018	0.3014	-0.0004

There can be no question, therefore, of the necessity for precautions to avoid loss of potassium perchlorate through solubility beyond that of using an alcoholic solution of perchloric acid as washing liquid. Finally we made a series of experiments under varied conditions in an effort to discover the procedure best adapted to yield accurate results. In all these experiments an exactly weighed quantity of potassium perchlorate, together with an approximately weighed portion of sodium perchlorate, was dissolved in water and the solution was evaporated to dryness with a small quantity of perchloric acid. In Expt. 28, Table III, the residue was extracted at 0° with an alcoholic solution of perchloric acid, and then was washed by decantation and transferred to the platinum-sponge crucible with chilled washing liquid. The excess in weight of recovered potassium perchlorate is undoubtedly due chiefly to mechanical inclusion, since the precipitate was not redissolved in the course of the washing.

In Expts. 29, 30 and 31, the dry residue was first extracted at 0° with washing liquid, and after 3 rinsings with washing liquid it was dissolved in water and the solution was evaporated to dryness with a little perchloric acid. A second extraction and rinsing with washing liquid followed. These experiments were comparable with those in the last table of our previous paper. As is to be expected, a consistent error persists, although somewhat less in magnitude than that indicated in the earlier results. We attribute the difference, in part at any rate, to the better quality of the sodium perchlorate used in these experiments.

In Expts. 32 to 36 the initial extraction of the dry salt was done with alcohol containing 0.1% of perchloric acid. Otherwise the experiments were identical with the preceding 3. The excess in weight of recovered perchlorate may be ascribed to either adsorption or inclusion of the sodium salt by the precipitate, rather than to salting out of material from the mother liquor.

Three additional rinsings of the first precipitate before solution and re-evaporation produced no perceptible effect on the results in Expts. 37 and 38.

In Expts. 39 and 40 the precipitate was dissolved and the solution evaporated after the third rinsing, and again after the fifth, washing liquid being used always, except in the initial extraction. This procedure, though troublesome, diminished the positive error to a point which for most purposes is very satisfactory.

In Expts. 41 and 42 the initial extraction with alcoholic perchloric acid was followed by 2 rinsings with the same liquid, but the precipitate was only once re-dissolved. The results compare favorably with those of the preceding 2 experiments, owing possibly in part to compensation between solution of the precipitate in the first 2 rinsings and inclusion.

TABLE III.

Expt.	First ext. act. Cc.	Washings. Cc.	NaClO ₄ taken G.	KClO ₄ taken, G.	KClO ₄ found, G.	Error, G.
28.....	A 20	W 95	0.1	0.3030	0.3038	+0.0008
29.....	W 20	W 110	0.3	0.3012	0.3017	+0.0005
30.....	W 20	W 110	0.5	0.3003	0.3009	+0.0006
31.....	W 20	W 107	1.0	0.3035	0.3044	+0.0009
32.....	A 20	W 118	0.1	0.3003	0.3005	+0.0002
33.....	A 20	W 100	0.1	0.3021	0.3023	+0.0002
34.....	A 20	W 105	0.3	0.3021	0.3025	+0.0004
35.....	A 20	W 95	0.5	0.3003	0.3007	+0.0004
36.....	A 20	W 95	1.0	0.3013	0.3019	+0.0006
37.....	A 20	W 100	0.5	0.3006	0.3009	+0.0003
38.....	A 20	W 108	1.0	0.3009	0.3016	+0.0007
39.....	A 20	W 102	0.5	0.3010	0.3012	+0.0002
40.....	A 20	W 100	1.0	0.3007	0.3010	+0.0003
41.....	A 20 + 10 + 10	W 85	0.1	0.3013	0.3012	-0.0001
42.....	A 20 + 10 + 10	W 77	1.0	0.3019	0.3023	+0.0004

In view of the foregoing evidence we, therefore, reiterate our earlier recommendations, with the modification that the initial extraction of the sodium perchlorate be carried out with alcohol containing perchloric acid but no potassium perchlorate, instead of with a saturated solution of the latter substance. In case the quantity of sodium is small, the use of a saturated solution of potassium perchlorate for the initial extraction is safe; in case the quantity of sodium is large, the potassium salt is best washed once or twice with alcohol containing perchloric acid before the use of saturated solution of the precipitate is commenced.

Aside from the above the chief recommendations are as follows:

1. The use of absolute alcohol.
2. The use of a low temperature in washing (0°).
3. The use of a platinum-sponge crucible.
4. At least one solution of the precipitate in water and re-evaporation in the course of the washing.

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5. The use of alcohol containing perchloric acid and saturated with potassium perchlorate at the temperature of use for washing the precipitate after the sodium salt has been extracted with alcohol containing perchloric acid.

The saturated solution of potassium perchlorate is best prepared by dissolving the necessary amount of salt in hot conc. aqueous solution of perchloric acid and adding the solution to anhydrous alcohol.

By this procedure the error can undoubtedly be kept within a very few tenths of a milligram, and seems to us preferable to, although more troublesome than that of Gooch and Blake, who have advocated the procedure of keeping the volume of washing liquid, consisting of an alcoholic solution of perchloric acid, very small. The errors in their experiments varied from negative values of from 0.5 to 0.9 mg. in the absence of sodium salts, to positive values up to 2.6 mg. in the presence of sodium salts.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORIES OF SOIL FERTILITY, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

COLORIMETRIC DETERMINATION OF TITRATION CURVES WITHOUT BUFFER MIXTURES.

BY LOUIS J. GILLESPIE

Received February 4, 1920

The writer is led to present this material by the experience of the late Dr. E. H. Walters (First Lieutenant, Sanitary Corps) and Dr. L. E. Wise, formerly in this laboratory, who found the titrimetric determination of molecular weight to be very useful in the identification of small quantities of unknown acids in cases where phenolphthalein could not be used and where no neutralization equivalents were given in the literature. The usefulness of the titration curves has been explained by Hildebrand,¹ who gave a comparatively simple electrometric procedure. The writer has aided both Dr. Wise and Mr. R. N. Harger in determining titration curves colorimetrically, using the assortment of indicators recommended by W. M. Clark and Lubs², and the 0.05 *M* buffer mixtures studied by them.³ For titration curves a large number of buffer mixtures were required, and we in fact resorted only to the colorimetric method because the neutralization equivalent was required for an organic acid containing arsenic, which badly poisoned the hydrogen electrode. Since that time the writer has developed a system for the colorimetric determination of

¹ THIS JOURNAL, 35, 847 (1913).

² H. A. Lubs and W. Mansfield Clark, *J. Wash. Acad. Sci.*, 6, 481 (1916); W. M. Clark and H. A. Lubs, *J. Bact.*, 2, 1, 109, 191 (1917).

³ W. M. Clark and H. A. Lubs, *J. Biol. Chem.*, 25, 479 (1916); also described in *J. Bact.*, *loc. cit.*

hydrogen ion concentration which requires no buffer mixtures,¹ and the main inconvenience for the present purpose is thereby removed. The procedure requires now little beyond the indicators themselves, and may be taken up without special preparation.

The data upon which Table I was constructed were determined by means of Clarks and Lubs' buffer mixtures,² the hydrogen-ion exponents of which were determined at the working room temperature, and the data were smoothed by the use of the equation $P_H = k + \log (\text{alk. form})/(\text{acid form})$, where P_H is the hydrogen ion exponent of Sørensen; k , the apparent or total dissociation constant, the logarithms are common, and "alk. form" and "acid form" are the concentrations of indicator practically completely transformed into the alkaline or acid form by excess of base or acid. The equation was verified for all the indicators of Table I within the limits of experimental error. The equation is the general equation of which Equation 7, page 1122, of Stieglitz³ is the type, and comes from the application of the mass-action law to both the dissociation and any tautomeric equilibria when the indicators are assumed to be monobasic acids or monacid bases. The values obtained from Table I should be good to about 0.1 at room temperatures (25 to 30°). Reference may be made to the other forthcoming paper for further details and literature discussion.

Neutralization equivalents are seldom given in the literature for cases where phenolphthalein or methyl orange cannot be used, yet such values can still be obtained in many cases by titration to the proper end-point, expressed in terms of hydrogen ion exponent (P_H). A titration curve shows the point, if there is any, where the largest change of reaction (P_H) occurs per drop of alkali (or acid) and this is the end-point of the titration. This point is taken as the middle of the steep or comparatively steep portion of the curve. The method can be applied for learning whether the acidity of a given mixture, perhaps of weak and strong acids, or of weak acids and salts of weak bases, can be determined by direct titration. A. B. Clark and Lubs⁴ recently gave a method for titrating 2 acids successively in the same solution in certain cases; other cases can be studied most directly by means of titration curves. The determination of the titration curve as outlined gives both the titration result required and at the same time information sufficient for the specification of conditions for simple titration and for the statement of the experimental error due to uncertainty of end-point.

¹ To be published in *Soil Science*.

² W. M. Clark and H. A. Lubs, *J. Biol. Chem.*, 25, 479 (1916); also described in *J. Bact.*, *loc. cit.*

³ *THIS JOURNAL*, 25, 1112 (1903).

⁴ *Ibid.*, 40, 1443 (1918).

Preparation of Indicator Solutions.

The indicators used are from the assortment recommended by Clark and Lubs,¹ after careful study in various biological fluids, in comparison with direct electrometric measurement. Some of them have also been tested in the same way in soil extracts,² of very low salt content. They are known to be a relatively high degree of reliability. With the exception of methyl red, they are sulfonphthaleins, a series which is the subject of an interesting series of papers by Dr. S. F. Acree and collaborators,³ who have been studying especially the seat of color change, and the various tautomeric and dissociation constants involved.

TABLE I.—DATA FOR THE DETERMINATION OF HYDROGEN ION EXPONENT.
Hydrogen ion exponent for each pair of tubes

Drop ratio.	Brom-phenol blue.	Methyl red	Brom-cresol purple	Brom-thymol blue	Phenol red	Cresol red.	Thymol blue
1 : 9.....	3.1	4.05	5.3	6.15	6.75	7.15	7.85
1.5 : 8.5.....	3.3	4.25	5.5	6.35	6.95	7.35	8.05
2 : 8.....	3.5	4.4	5.7	6.5	7.1	7.5	8.2
3 : 7.....	3.7	4.6	5.9	6.7	7.3	7.7	8.4
4 : 6.....	3.9	4.8	6.1	6.9	7.5	7.9	8.6
5 : 5.....	4.1	5.0	6.3	7.1	7.7	8.1	8.8
6 : 4.....	4.3	5.2	6.5	7.3	7.9	8.3	9.0
7 : 3.....	4.5	5.4	6.7	7.5	8.1	8.5	9.2
8 : 2.....	4.7	5.6	6.9	7.7	8.3	8.7	9.4
8.5 : 1.5.....	4.8	5.75	7.0	7.85	8.45	8.85	9.55
9 : 1.....	5.0	5.95	7.2	8.05	8.65	9.05	9.75
% in indicator solution.....	0.008	0.008	0.012	0.008	0.004	0.008	0.008
Cc. 0.1 N NaOH per 0.1 g. portion.....	1.64	..	2.78	1.77	3.10	2.88	2.38
Produce acid color with.....	0.05 N HCl	0.05 N HCl	0.05 N HCl	0.05 N HCl	0.05 N HCl	2% H ₂ KPO ₄	2% H ₂ KPO ₄ or H ₂ O
Quantity acid used to produce acid color..	1 cc.	1 drop	1 drop	1 drop	1 drop	1 drop	1 drop

The strengths given in Table I are suitable for test-tubes of about 15 mm. external diameter with moderately thin wall. The test-tubes should be of fairly uniform diameter and should have no flanges. Methyl red solution is made up in alcohol of about 60 vol. per cent. The free indicator acid is dissolved in acid-free alcohol after grinding and the volume made up with distilled water (6 volumes of alcoholic solution being made up to 10). The other indicators are prepared as monosodium salt in

¹ H. A. Lubs and W. Mansfield Clark, *J. Wash. Acad. Sci.*, 6, 481 (1916); W. M. Clark and H. A. Lubs, *J. Biol. Chem.*, 2, 1, 109, 191 (1917).

² L. J. Gillespie, *J. Wash. Acad. Sci.*, 6, 7 (1916); L. J. Gillespie and Lewis A. Hurst, *Soil Science*, 6, 219 (1918).

³ *THIS JOURNAL*, 41, 1190 (1919), and previous articles.

water solution, 1.1 equivalents of alkali being used except in the case of dibromo-*o*-cresolsulfonphthalein, which requires more nearly 1.5 equivalents.¹ The strengths given are in terms of the free acid. The table gives the quantity of standard alkali furnishing the stated number of equivalents for 0.1 g. portions of the indicator acids. In dissolving the indicators, it is practically necessary to grind the indicator with the alkali, added in portions, before making up the volume. Heat may be used, but should be unnecessary. The indicator solutions are reasonably permanent, but the color standards prepared from them should not be trusted more than a day or so, especially the more alkaline indicators.

The indicators can now be purchased in this country or prepared.²

Preparation of Color Standards and Use in Determination of Hydrogen Ion Exponent.³

A very similar technique has been proposed by Barnett and Chapman⁴ for determination of hydrogen ion exponent with phenol-sulfonphthalein.

To take a concrete example, if 6 drops of methyl-red solution be put in a test-tube with the addition of a drop of dil. alkali and enough water to make the volume 5.5 cc., and 4 drops of methyl-red solution be treated in another test-tube with a drop of dil. acid and enough water to bring the liquid to the same height (the tubes should be nearly uniform), this pair of tubes constitutes a color standard, such that a solution of unknown hydrogen ion exponent containing 10 drops of indicator solution in the same volume will have the exponent 5.2, if its color, viewed through the side, matches the color seen when the light passes through both tubes of the standard pair held together (conveniently with rubber bands). The figure 5.2 is found from Table I, under the heading methyl red and opposite the drop ratio 6 : 4. The first figure of the drop ratio indicates the number of drops in the alkaline tube, and the second the number in the acid tube of the color standard pair. To secure a better optical effect a tube of clear water should be held behind the tube containing the unknown solution. The simple comparator shown in Fig. 1 (modified from the comparators used by Hurwitz, Meyer, and Ostenburg⁵ and by Clark and Lubs⁶ is of great convenience, and almost necessary if the unknown solution is colored itself. In this case some of the unknown without in-

¹ Dr. H. A. Lubs, private communication.

² H. A. Lubs and W. M. Clark, *J. Wash. Acad. Sci.*, 5, 609 (1915); and 6, 431 (1916); E. C. White and S. F. Acree, *THIS JOURNAL*, 41, 1190 (1919), and previous articles.

³ The hydrogen-ion exponent is the common logarithm of the reciprocal of the hydrogen ion concentration in gram equivalents per liter. As the solution becomes more alkaline, the exponent increases, passing through about 7.0 at physico-chemical neutrality.

⁴ *J. Am. Med. Assoc.*, 70, 1062 (1918).

⁵ *Johns Hopkins Hospital Bull.* 27, 16 (1916).

⁶ W. M. Clark and H. A. Lubs, *J. Bact.*, 2, 1, 109, 191 (1917).

indicator is put in a test-tube back of the standard pair for compensation, and 2 tubes of clear water in back of the unknown plus indicator. This is the device of Walpole,¹ who also studied the titration curve of solutions which had themselves indicator properties. In this case standard

alkali (or acid) is added to the unknown solution without indicator, just as it is added in the actual titration. The comparator illustrated is suitable for test-tubes of the above given dimensions.

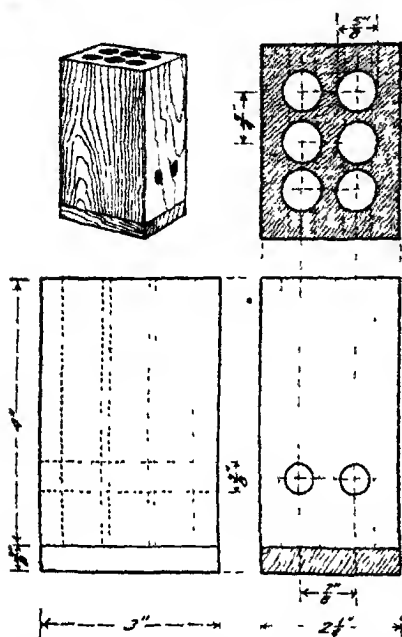


Fig. 1.—Comparator for hydrogen ion exponent measurements. The interior is painted black.

Table I gives the necessary data. The first figure of the drop ratio indicates the number of drops in the alkaline tube, and the second, the number in the acid tube of the color standard pair. The ratios 1.5 : 8.5 and reverse are included because of their occasional usefulness. Three and 17 drops are taken and the volume is made up two-fold, i. e., to 11 cc. Extra ratios may be interpolated at will in this way wherever desired. The quantities of acid used to develop the full acid color in the standards need not be exact, even as to the number of drops. For producing the full alkaline color in the standards, one drop

of 0.05 *N* NaOH is satisfactory, except for thymol blue, which requires 2 or 3 drops.

The indicators are entered in the table under their laboratory names: their chemical names being, in regular order: tetrabromophenol-sulfonphthalein, 4'-dimethylamido-azobenzene-2-carboxylic acid, dibrom-*o*-cresol-sulfonphthalein, dibromo-*o*-thymol-sulfonphthalein, phenol-sulfonphthalein, *o*-cresol-sulfonphthalein, and thymol-sulfonphthalein.

Titration Procedure.

A definite quantity of substance is made up to definite volume with water,² and aliquot portions are used, one for each necessary indicator.

¹ *Biochem. J.*, 5, 207 (1910)

² If the solution is not aqueous, but contains much alcohol or other solvent, the figures of Table I cannot be expected to apply. However, it still may be possible to

If the substance is rare, one portion may serve sometimes for 2 indicators, as detailed below. The indicators may be used in regular order for the complete curve, but generally the approximate turning point will be known well enough to avoid the necessity for using all, and the curve is constructed in sections, which may, of course, be determined in any order. A chosen indicator solution is added to the aliquot in the proportion of 2 drops per cc. of the aliquot. Standard alkali (or acid) is then added until the color begins to change. Two drops of indicator solution are then added for every cc. of standard alkali added, and, after mixing, a portion of the solution is poured into a test-tube and its hydrogen ion exponent determined by means of the color standards. The solution is then returned to the main portion, without rinsing the test-tube, more alkali is added until the color has changed significantly, and indicator solution is added as before and the exponent determined in the same test-tube. As the titration proceeds, the hydrogen ion exponents are plotted vertically on cross-section paper against the number of cc. of standard alkali (or acid) added. The titration is continued until the indicator has reached its limit. Another section of the curve is then secured by the use of another indicator. It is sometimes possible to economize valuable substance by applying 2 indicators in succession to the same solution; for this, the working ranges of the 2 must not overlap. In this way we have used phenol-sulfonphthalein after methyl red. Before the alkaline limit for methyl red was reached the curve had already become steep, so that a slight excess of alkali sufficed to bring the reaction into the phenol-sulfonphthalein region. It was desired to obtain more of the curve in order better to estimate the middle point. Methyl red solution was, therefore, diluted in water containing a drop of alkali, 2 drops of methyl red per cc., and this was placed in the comparator in back of the phenol-sulfonphthalein color standard. Phenol-sulfonphthalein was added to the aliquot used for methyl red, and the titration continued with the phenol-sulfonphthalein color standards.

The procedure for colored bodies, including such as may possess indicator properties, was outlined above under the preparation of the color standards.

The method has certain limitations. The data do not extend into the alkaline region beyond the useful range of phenolphthalein. If desired, phenolphthalein may be used in the same way as the others. It has the disadvantage of a relatively high salt error, as was shown by the work of

carry out the scheme with satisfaction, even if the various curve-portions found for the different indicators do not fit together, since the sudden change in the form of the titration curve may occur almost entirely within the range of one indicator. There are many cases where hydrogen ion determinations may be very serviceable, in solutions hardly aqueous, whether or not the absolute P_{H} values are greatly in error.

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Rosenstein.¹ He gave figures for various salt contents, for which reference must be made to his article. For the case where the salt content is 0.05 *N*, and the temperature 23–24°, the following hydrogen ion exponent values may be used. For the successive drop ratios, 1 : 9, 2 : 8, 3 : 7, 4 : 6, 5 : 5, 6 : 4, 7 : 3, the values are 8.8, 9.1, 9.2, 9.3, 9.5, 9.7, 9.8, respectively. An 0.08% solution of phenolphthalein in alcohol is suitable. The values are calculated from the data of Rosenstein, but are modified by subtracting 0.1 in every case, in accordance with some measurements of the writer.

Another limitation relates to the possible inexactness of the method if applied to solutions containing substances which may have specific action on the dissociation or tautomerism of the indicators. The method may still be of sufficient value, however, as in solutions containing organic solvents, as discussed in a footnote under "Titration Procedure."

In case the removal of carbon dioxide is necessary, this should be done at room temperature, by passing air through soda lime and then through the solution.

Summary.

A simple method has been described for securing titration curves colorimetrically, which requires the minimum of equipment. The hydrogen ion exponents are determined without the use of buffer mixtures. Instead of a buffer mixture containing indicator, a color standard is used, consisting of a pair of test-tubes containing together 10 drops of indicator solution of suitable strength, the drop ratio being varied from 1 : 9 to 9 : 1. One tube of the pair contains dil. alkali and the other contains dil. acid. Reference to a table gives the hydrogen-ion exponent corresponding to the drop ratio, or the exponents can be calculated from the relation $P_H = k + \log (\text{drop ratio})$; where the logarithms are common, the drop ratio is the ratio of the number of drops (of the indicator solution) in the alkaline tube to the number in the acid, and the values of k (good to about 0.1 at 25–30°) are the following: tetrabromo-phenol-sulfonphthalein, 4.1; methyl red, 5.0; dibromo-*o*-cresol-sulfonphthalein, 6.3; dibromo-thymol-sulfonphthalein, 7.1; phenol-sulfonphthalein, 7.7; *o*-cresol-sulfonphthalein, 8.1; thymol-sulfonphthalein, 8.8. Details of technique are given in full.

WASHINGTON, D. C.

¹ THIS JOURNAL, 34, 1117 (1912). The writer has no definite comparison to offer for the relative values of thymol blue and phenolphthalein. No systematic study of the salt errors of thymol blue has yet appeared such as Rosenstein's study of phenolphthalein. Clark and Lubs studied thymol blue in solutions of various composition. The study in soil extracts has not been extended to cresol red or thymol blue. Furthermore, the titration curves determined hitherto in this laboratory have not included these 2 indicators. We suspect that calcium hydroxide may exert a specific action upon them, but have not settled the point. We used sodium hydroxide.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

CATALYTIC HYDROGENATION WITH PROTECTED HYDROSOLS.

BY ERIC K. RIDEAL.

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Applications of colloidal platinum and more especially of colloidal palladium as catalytic hydrogenating agents have now become general in many organic syntheses. The hydrosols prepared by reduction with hydroxylamine salts are usually protected by Paal's method with the sodium salts of protalbic and lysalbic acids. These colloids have been used by Paal and his co-workers¹ in a great variety of reduction processes but other protective colloids possessing low gold numbers such as gelatine, gum arabic, or casein may be employed.

Catalysts prepared according to Paal's method are found to be extraordinarily stable both towards temperature changes and to the presence of electrolytes, but they are very variable in activity. It was formerly thought² that the protective effect of the colloid was due to mutual absorption, resulting in the formation of a coating over the metal surface by the protective colloid, while Bancroft³ identifies protective action with peptization, indicating the disintegrating or peptizing action of the protective colloid in a great number of instances.

When colloidal sols are employed for catalytic purposes the choice between Freundlich's theory and that of Bancroft as to the mechanism of protection becomes one of great importance. According to Freundlich's point of view the activity of a colloidal catalyst should fall on the addition of the protecting agent since the active surface of the catalyst become covered with the inert protector. On the theory of peptization, on the other hand, the addition of small amounts of the protective agent should peptize the colloid metal and thus increase its surface and consequently its activity should rise; after the addition of the optimum amount of peptizing agent, this amount being governed by various factors such as the magnitude of the various interfacial surface tensions and the viscosity of the medium which affects the Brownian movement, the metal sol is peptized as far as possible. Subsequent addition of the peptizing agent can now no longer increase the surface of the sol but will commence to cover up the free surface of the metal, with a consequent decrease in catalytic activity.

It appeared probable that this preliminary rise and subsequent fall in catalytic activity on the progressive addition of a protective colloid, which was to be anticipated on Bancroft's hypothesis should be capable of experimental determination; such was found to be the case in the cata-

¹ *Ber.* (1902); especially *Ber.* 39, 26 (1904); 41, 818 and 2281 (1908); 42, 2239 (1909); 48, 994 (1915).

² Freundlich, "Kapillarchemie," p. 455.

lytic reduction of phenyl propiolic acid utilizing both platinum and palladium hydrosols with gum arabic as protective colloid.

Influence of Concentration of Peptizing Agent.

The general method of procedure was as follows. Ten cc. of a solution of palladium or platinum chloride containing 10 mg. of the metal was carefully neutralized with sodium carbonate and to the solution a known amount of gum arabic was added in the form of a solution containing one mg. per cc.; the salt was subsequently reduced with hydroxylamine prepared from hydroxylamine sulfate. To the protected sol 10 cc. of a solution of the sodium salt of phenyl-propionic acid was added, the salt being prepared from the pure acid and the solution containing 14.8 g. per liter of the acid. The mixture of protected sol and sodium phenylpropionate was then run into an Erlenmeyer flask and shaken continuously in an atmosphere of hydrogen, prepared by electrolysis of a solution of sodium hydroxide and from which all traces of oxygen had been carefully removed. The rate of absorption of the hydrogen was measured by the rate of flow of water from a buret into a small Erlenmeyer flask connected with the absorption vessel and a manometer. The experiments were conducted at 15° and a blank run of 4 hours duration indicated that the rate of diffusion of the hydrogen through the flexible rubber connection was negligible. The rates of absorption with various amounts of gum arabic as protective colloid are indicated in the following curves, each representing the mean of 3 experiments. As typical of one determination the following may be cited:

Catalyst, 10 mg. Palladium Protected with 2 mg. of Gum Arabic Temp. 15°

H	Time		l	Cc. of water run into compensate for contraction
	m	s		
1	2	50	0	0
	27	20	2 2	10
	28	16	3 6	15
	30	0	5 0	20
	31	42	6 7	25
	33	30	8 5	30
	35	0	10 0	35
	36	54	11 9	39
	38	48	13 8	43
	40	54	15 9	47
	43	18	18 3	51
	46	0	21 0	55
	50	18	25 3	60
	54	30	29 5	64
	58	30	33 5	68
2	3	0	38 0	72
	8	30	43 5	76
	16	18	51 3	80

It will be noted that there is an optimum concentration of gum arabic for each catalyst, 2 mg. per 10 mg. for palladium and for the like amount of platinum 4 mg. is required; since the atomic weight of platinum is practically twice that of palladium this latter metal is peptized 4 times as easily as the former. It seems probable however that the phenylpro-

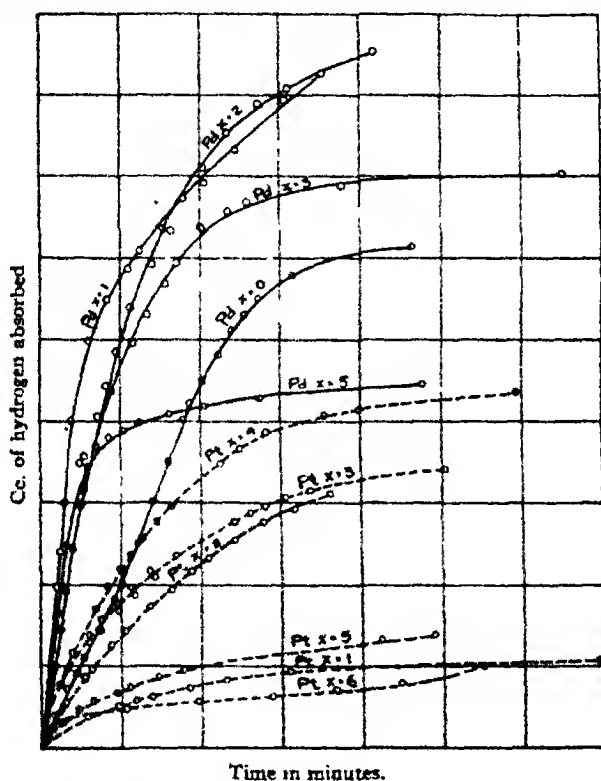


Fig. 1.

x = mg. of gum arabic per 10 mg. of metal.

piolic acid assisted in the peptizing of the colloid, since, when only small concentrations of gum arabic were employed, the sol would usually flocculate toward the end of the run, an indication that the unsaturated acid took part in the peptization but that the saturated acid was less active in this respect, an hypothesis in accord with the accepted views on the chemical nature of adsorption phenomena.

Influence of Promoters.

It has long been known that the addition of small quantities of similar

For this so-called promoter action there is as yet no adequate explanation and the study of the phenomenon has been confined chiefly to massive catalysts. It was, therefore, thought of interest to investigate the mutual effect of 2 somewhat similar substances platinum and palladium when reduced together in the sol form.

A series of runs was made in which 10 mg. of the mixed metals in various proportions were precipitated together in the sol form. As stabilizing colloid 3 mg. of gum arabic was employed, this concentration permitting each metal in the pure state to exert almost its maximum activity. The results of these experiments are depicted in Fig. 2.

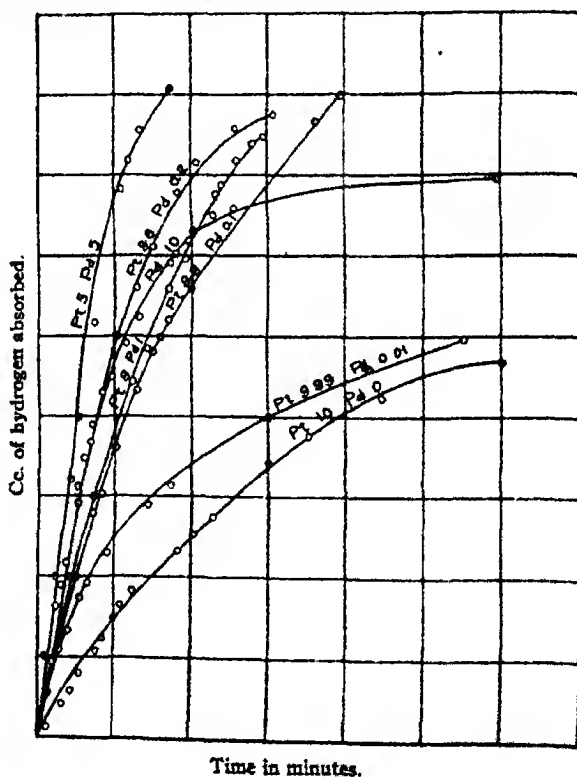


Fig. 2.

It was noted in all cases where the sol was prepared from the mixed metals, especially from platinum containing small quantities of palladium that there was a very marked improvement in stability and resistance to age over those prepared from the pure salts. This suggests the hypothesis that promoters may in part function as stabilizing agents.

catalysts, or for catalysts which pass through a colloidal stage at some point in their preparation.

For this reaction there is a steady increase in the catalytic activity of platinum sol on the addition of small quantities of palladium until a concentration by weight of 9.8 mg. of platinum to 0.2 mg. of palladium is reached. At this point it would appear that there is a slight decrease in activity until a ratio of 9 mg. of platinum to one mg. of palladium is reached followed by a rise to the ratio 5 mg. to 5 mg. which appears to be a maximum, the activity then slightly sinking for pure palladium. These latter differences are, however, so slight as to be within the region of experimental error, since such factors as the partial or complete removal of the carbon dioxide resulting from the neutralization of the acid chloride by means of sodium carbonate, the temperature of reduction and the age of the sol, all exert by no means inappreciable effects on the catalytic activity. It is evident, however, that a mixed sol containing about 9.8 mg. of platinum to 0.2 mg. of palladium (atomic ratio 26 to 1) is practically as active as a pure palladium sol in the hydrogenation of phenyl-propionic acid.

The curves obtained in the first 2 series of experiments represent the combined effects of 2 reactions, the absorption of hydrogen by the metal and the hydrogenation of the acid. The experiments of Paal and Gerum¹ indicated that the precipitated sol protected with sodium protalbate and brought into the sol form again with a trace of alkali took up relatively small quantities of hydrogen, the figures obtained approximating to the composition PdH for palladium black to $\text{Pd}(\text{H})_2$ for the protected sol under a pressure of one atmosphere of hydrogen. Experiments with the sols of palladium and platinum protected with small quantities of gum arabic, and which had not been precipitated and reprecipitated indicated that under these conditions very much larger quantities of hydrogen could be taken up: thus a mixture of 9 mg. of platinum and one mg. of palladium prepared by direct reduction in the presence of 3 mg. of gum arabic absorbed 80 cc. while 5 mg. of platinum and 5 mg. of palladium absorbed 106 cc. of hydrogen, equivalent to the formation of the hypothetical compounds $\text{Pd}(\text{H})_{10}$ and $\text{Pt}(\text{H})_{10}$ under one atmosphere pressure. (A large excess of hydroxylamine was not used in the precipitation of the sols.) It is interesting to note that the atomic absorption of both platinum and palladium under these conditions is identical.

A number of experiments in which the hydrogen absorption curves were obtained first for the metal sol and then for the hydrogenation of the sodium phenyl-propionate which was subsequently added to the hydrogenated sol indicated that the hydrogenation of the sol took place relatively quickly and at the same speed for both platinum and palladium while the curves

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quent hydrogenation of the unsaturated acid proceeded rapidly in the case of palladium and but slowly in the presence of platinum, as is instanced by the following figures.

Catalyst: 10 Mg. Platinum				10 Mg. Palladium			
Time. Min.	Cc. H ₂ absorbed by catalyst	Time. Min.	Cc. H ₂ absorbed by acid	Time Min	Cc. H ₂ absorbed by catalyst	Time Min	Cc. H ₂ absorbed by acid
0	0	0	0	0	0	0	0
1.5	4	6.5	2	1.5	12	1	20
3	8	14	4	3.0	24	2.5	28
4.3	12	20.5	6	4.1	36	3	35
5.5	16	29	8	5	40	4	40
7.3	20	37	10	5.5	48	7.5	43
11.5	28			9	56	15	45
16	36			11.5	60	20	45.7
21	44			20	68		
26	52			32	74		
34	60			41	78		
42.5	68			48.5	80		
52.5	76						

Catalyst: 5 Mg. Palladium		5 Mg. Pt		9 Mg. Platinum		1 Mg. Palladium	
Time	Cc. H ₂	Time	Cc. H ₂	Time	Cc. H ₂	Time	Cc. H ₂
0	0	0	0	0	0	0	0
1.2	8	1.5	8	2	12	2	8
4.5	20	3.2	16	4.75	20	3.5	12
7.5	28	5	24	7.75	28	5.5	16
10.5	36	7.3	32	11.25	36	7.5	20
13.5	44	9.5	40	16	44	15	28
17.3	52	11.7	48	22.3	52	20	32
22	60	15	51	30.75	60	27	36
27	68	20	52	44	68	31	38
34	76	30	53	52	70	36	40
43.5	84						

It will be noted that all the curves are of the same type, linear over a great part of their course approaching logarithmic towards the end. This type of curve appears to be general for a large number of colloidal catalytic processes. Bredig and von Bernick and Groh¹ found in the decomposition of hydrogen peroxide with colloidal platinum, both unprotected and protected that the family of decomposition-time curves obtained could be represented by the relationship $dx/dt = K(a - x)$ where a is the initial and x the concentration of peroxide at a time t . This expression holds for a monomolecular chemical reaction or for a process in which diffusion is operative. That the diffusion is an important factor is seen from the work of Groh who found that the K values lessened with progressive addition of gelatin to the platinum sol, but showed, however, the usual irregularities noted above. Paal's values for the hydrogenation of cinnamic acid²

¹ *Z. phys. Chem.*, 88, 414 (1914).

² *Ber.*, 41, 2276 (1908).

in a constant pressure hydrogen atmosphere also show a general approximation to a curve of the above type, while if his values for the combination of hydrogen and ethylene (equal volumes) in the presence of colloidal platinum and palladium¹ be plotted, it will be found that the curve, in the case of a fresh palladium sol, approximates to a bimolecular reaction, and with platinum between a bi- and a monomolecular reaction.

F. Armstrong and Hilditch² found that the absorption time curves for the hydrogenation of various unsaturated glycerides in the presence of colloidal nickel, were nearly linear and showed distinct curvature only when saturation was nearly completed. These observers came to the conclusion that a great part of the absorption curve could be represented by the expression $dx/dt = K$ and inferred that a nickel oleate adsorption complex of constant active mass was formed, the observed rate of reaction being that of the less reactive hydrogen under constant pressure reacting with the complex; the subsequent falling off in the rate being due to the interference by the saturated glyceride formed in the process. The following figures indicated a few of the values of K as calculated from the expression $dx/dt = K(a - x)$ for the hydrogenation of phenylpropionic acid.

Catalyst, 10 Mg of Platinum 10 Mg of Palladium 9.5 Mg of Platinum, 0.5 Mg of Palladium protected with 3 Mg of Gum Arabic

Time, M	x	K	Time	x	K	Time	x	K
10	0	0.0090	5	20	0.0183	5	14	0.0129
20	16.2	0.0089	10	32	0.0158	10	20.5	0.0130
30	21.6	0.0086	15	41.5	0.0162	15	36	0.0127
40	26	0.0085	20	46.7	0.0128	20	44	0.0124
50	30.7	0.0088	30	57	0.0112	30	53.5	0.0109
60	35	0.0094	40	64	0.0102	50	62.3	0.0085
70	37.5	0.0094	50	66.7	0.0089	60	64.9	0.0060
80	41.2	0.0099	60	68.2	0.0076	70	66.5	0.0067
100	44.8	0.0176	80	69	0.0066	80	67.5	0.0060
			80	69.5	0.0060			

It would appear from an analysis of these various examples that the rate of chemical reaction at the protected colloid surface is not governed so much by the formation of a colloid-reactant complex to which the other reactant diffuses and reacts with it but primarily by the rate of diffusion of both of the reactants to the colloid surface, thus in the case of the decomposition of hydrogen peroxide or in the various hydrogenating reactions under constant hydrogen pressure the reactions approximate to a monomolecular chemical reaction in form, being in reality a diffusion process. In the ethylene hydrogen reaction, where the reaction is governed by the rate of diffusion both reactants a pseudochemical bimolecular

¹ *Ber.*, 48, 994 (1915); 42, 2239 (1909).

² *Proc. Roy. Soc.*, 96A, 137 (1919)

reactant results. The values of K , the reaction velocity coefficient or the diffusion coefficient can, however, be made extremely small by coating the colloid with a relatively thick layer of protective colloid.¹ by using as reaction medium a very viscous substance having a low diffusion coefficient such as oil, or by employing reactants which diffuse very slowly.

For small values of K the alteration in the reaction velocity dx/dt with the alteration in the concentration of the reactant in the environment ($a - x$) will be inappreciable, and the curves will degenerate into the limiting form $dx/dt = K$ over a very considerable range of their existence. This phenomenon is likewise noted with old colloidal sols where the active surface is presumably well coated. A progressive deterioration in the type of curve is noted in the following cases, hydrogen peroxide, ethylene, cinnamic acid, phenylpropionic acid and glyceryl oleate, coinciding with a decrease in the value of the diffusion coefficients.

The values of K obtained in this manner are, however, only very approximate, since there may ensue an alteration in the effective surface of the catalyst during the reaction, either an increase² due to continued peptization of the colloid during the reaction or more generally a decrease, as noted in a variety of reactions. This decrease is in part due to the presence of the products of the reaction lowering the rate of diffusion of the reactants to the surface³ but it may also be due to the products of the reaction becoming absorbed to the surface of the catalyst as suggested by Langmuir, and thus decreasing the effective catalytic area. It is, however, to be expected, that the form of curves obtained may be interpreted on either of these hypotheses with equal facility.

Summary.

The effect of a protective colloid on the reaction velocity of a hydrogenation process in the presence of colloidal platinum and palladium has been studied and the results lead to the conclusion that the protective colloid functions as a peptizing agent, in agreement with Bancroft's hypothesis.

The addition of a small quantity of a palladium sol to a platinum sol greatly enhances its activity, and it is suggested that promoter action may in part be due to peptization.

The mechanism of catalytic actions in the presence of colloidal metal appears to conform rather to the diffusion hypothesis than to the colloid reactant complex theory. Abnormalities are equally explicable on the single layer theory as on the view that the retardation of diffusion is caused by the products of the reaction.

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¹ See Groh, *loc. cit.*, and Fig. 1.

² Expt. 1; and Groh, *loc. cit.*

³ Armstrong and Hilditch, *loc. cit.*; Fink, on the oxidation of SO_2 ; Bodenstein and Ohlmer on the oxidation of CO .

POTASSIUM CHLORATE AS A STANDARDIZING SUBSTANCE FOR SOLUTIONS OF ALKALI.¹

BY H. B. VANVALKENBURGH.

Received February 11, 1920.

Introduction.

Many substances have been proposed for the standardization of a solution of an alkali. Glaser² mentions, among others, oxalic acid, potassium tetroxalate, potassium hydrogen tartrate and potassium hydrogen iodate. Except oxalic acid these substances are not well suited for this purpose, since they cannot be prepared in a state of purity so that it is certain that their actual composition agrees with their theoretical composition. Potassium hydrogen tartrate contains impurities and does not give strictly accurate results. Potassium hydrogen iodate contains no water of crystallization, but it must be carefully examined qualitatively for chlorides, chlorates, free chlorine and hydrogen chloride before it can be used; also it is not a common salt. Phelps and Weed³ proposed the use of certain organic acids and anhydrides—benzoic, malonic, succinic and phthalic acids and succinic and phthalic anhydrides. An objection to the use of organic acids is that some of them are only slightly soluble, which necessitates the use of somewhat bulky solutions. Furthermore, the results obtained by Phelps and Weed were not concordant. For example, with succinic acid the mean of 10 determinations differs as much as 15% from the theoretical value, while with phthalic and benzoic acids there is a difference of 12% and 16%, respectively, between the experimental and theoretical values. All of these results were higher than the theoretical value.

The Method.

A method which would be free from the objections to the various substances heretofore proposed, and yet give accurate and dependable results, would be desirable. This paper deals with a method proposed by Prof. C. G. Carroll (now deceased) and the work was carried out under his direction. The method is the reduction of potassium chlorate with sulfur dioxide and the standardization of the alkali with the definite amount of sulfuric acid thus formed. The equation which expresses the reaction may be written, $3\text{SO}_2 + \text{KClO}_3 + 3\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + \text{KCl}$. It will be seen that the method is a very simple one and that there are many advantages in its favor. Potassium chlorate can be obtained sufficiently pure by recrystallization, it contains no water of crystallization, it can be easily freed from any moisture without altering its composition, and only

¹ An abstract of part of a thesis submitted to the Graduate School of the University of Arkansas in partial fulfillment of the requirement for the Degree of Master of Science.

² "Indicatoren der Acidimetrie und Alkalimetrie," 1909.

³ *Z. anorg. Chem.*, 59, 114 (1908).

A small amount is necessary for one titration—from 0.6 to 0.9 g. for a normal solution.

The potassium chlorate used was dried for 6 hours at 170° and kept in a desiccator over phosphorus pentoxide, but the results obtained (Table III) seem to indicate that not all of the moisture had been driven off, so that in further work the salt was heated for 4 to 6 hours at 240° and more uniform results were obtained (Table IV). Stas had used potassium chlorate in determining the $\text{KClO}_3:\text{KCl}$ ratio. He fused the chlorate in order to free it from moisture, assuming that at the fusion temperature (357°) the salt undergoes no decomposition. But Stähler¹ found that when small quantities of potassium chlorate are fused rapidly, slight decomposition takes place, one g. losing about 0.02 mg. of oxygen; and when larger quantities (10 to 12 g.) are fused the loss is more considerable, about 0.4 mg. of chloride being formed for each g. of chlorate. The conclusion of Stähler is confirmed by the author's work, as shown in Table V.

Description of the Process.

Portions of the chlorate which had been previously dried, were weighed out and placed in 375 cc. Erlenmeyer flasks, 200 cc. water added, the solution boiled for 10 minutes, and a rather vigorous stream of sulfur dioxide passed into the boiling solution until all the chlorate was reduced. The excess of sulfur dioxide was then boiled off and the solution titrated, either hot or cold, against the alkali which was to be standardized. Phenolphthalein was used as indicator.

The solution was first boiled to expel all absorbed air and kept boiling to protect it from the air and thus prevent oxidation of any escaping sulfur dioxide. Various devices were used to insure against loss while boiling and the most satisfactory scheme was to boil the solution in unstoppered Erlenmeyer flasks. It was found that with samples not greater than one g. of chlorate, 30 minutes was long enough to reduce all the chlorate; it was also found that in some cases 20 minutes was not sufficient time to do this, so the gas was always passed in for 30 minutes. From 5 to 10 minutes was sufficient time to boil off the excess of sulfur dioxide. The sulfur dioxide was prepared by allowing conc. sulfuric acid to drop on to sodium hydrogen sulfite. The gas was allowed to run 5 minutes before being passed into the solution so as to free the apparatus from air.

Experimental.

An approximately normal solution of hydrochloric acid was made up and its strength determined by titrating against sodium carbonate prepared from the oxalate by slow and careful heating. The heating was done in platinum crucibles which were placed in beakers for the titration. A slight excess of acid was run in, the solution boiled to expel

¹ *Z. anorg. Chem.*, 71, 368 (1911)

carbon dioxide, and the excess acid determined by titrating back with sodium hydroxide whose relative strength was known. Phenolphthalein was used as indicator. The results are shown in Table I.

TABLE I
Standardization of HCl Against Na_2CO_3 (from $\text{Na}_2\text{C}_2\text{O}_4$)

	Oxalate G	Acid required Cc	Normality of acid.
1	1.4472	21.24	1.0165
2	1.8376	26.96	1.0169
3	2.1049	38.85	1.0165

Mean normality, 1.0163

Mean difference, 0.03%

An approximately normal solution of sodium hydroxide was prepared according to the method recommended by Cowles¹ and the relative strength of this solution determined by titrating against the standard acid, the solution being protected from the air by soda-lime tubes. The results are given in Table II.

TABLE II
Standardization of NaOH Against Standard HCl.

Series I			Series II		
Acid Cc	NaOH Cc	Acid equiv. to one cc. NaOH	Acid Cc	NaOH Cc	Acid equiv. to one cc. NaOH.
20.145	19.275	1.0451	20.20	19.33	1.0450
30.14	28.835	1.0452	30.14	28.85	1.0449
35.39	33.865	1.0450	36.16	34.60	1.0451
40.81	39.045	1.0452	40.19	38.445	1.0453
			44.21	42.31	1.0452
			48.24	46.045	1.0455

Mean, 1.04515

Mean, 1.04537

Mean of two series, 1.04525

Normality of NaOH, 1.06263

The sodium hydroxide solution was then standardized against potassium chlorate with the results given in Table III.

TABLE III.
Standardization of NaOH Against KClO_4 (dried at 170°).

	Chlorate used G	NaOH required Cc	Normality of NaOH.
1	0.96895	44.58	1.06398
2	1.3159	60.62	1.0626
3	0.6918	31.86	1.0630
4	0.8109	37.31	1.06403

Mean normality of NaOH, 1.06340

Normality against acid, 1.06263

Difference, 0.08%

It will be seen that the results given in Table III are slightly higher than those obtained against the acid. It was thought that this was due to the chlorate not having been entirely freed from moisture. To test

¹ THIS JOURNAL, 30, 1192 (1908)

this, the sample of chlorate used was heated for 4 hours at 240° , cooled, weighed out, reduced and titrated against the alkali solution, with the results as given in Table IV.

TABLE IV.
Standardization of NaOH Against KClO_3 (dried at 240°).

	Chlorate used, G.	NaOH required, Cc.	Normality of NaOH.
1.....	0.8117	37.41	1.0625
2.....	0.8085	37.25	1.06225
3.....	0.6750	31.085	1.0630
4.....	0.5091	23.465	1.0624
5.....	0.8970	41.305	1.0628
6.....	0.7112	23.78	1.0624

Mean normality of NaOH, 1.06255

Normality against acid, 1.06263

Difference, 0.008%

To see what effect fusing the chlorate would have upon the results, about 5 g. of the dried salt was placed in a quartz crucible and quickly fused, the operation requiring about a minute. Portions of this salt were then used to determine the normality of the alkali solution.

TABLE V.
Standardization of NaOH Against KClO_3 (fused).

Chlorate used, G.	NaOH required Cc.	Normality of NaOH.
0.6801	31.285	1.0642
0.7437	34.215	1.0641

Mean normality of NaOH, 1.06415

Normality against acid, 1.06263

Difference, 0.16%

It will be seen that the results are over 0.1% higher than the normality obtained by titrating against acid or dried but not fused salt. This may be accounted for by the fact that a small quantity of chloride was formed during fusion, which would cause the normality to be higher. The fused salt gave a distinct opalescence with silver nitrate, considerably more than did the salt which had been heated for 4 hours at 240° . Thus Stähler's results are confirmed.

Summary.

1. Solutions of alkali can be standardized against potassium chlorate with uniform results which agree closely with those obtained by standardizing against standard acid.

2. Potassium chlorate of sufficient purity for standardization can be prepared from the ordinary c. p. salt by recrystallization.

3. The best results are obtained by (1) drying the chlorate for 4 to 6 hours at 240° , (2) boiling the solution in an open Erlenmeyer flask, and (3) passing sulfur dioxide into the boiling solution for 30 minutes.

Boulder, Colo.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE ROYAL
POLYTECHNICAL INSTITUTE OF COPENHAGEN.]

STUDIES ON SOLUBILITY. I. THE SOLUBILITY OF SALTS IN SALT SOLUTIONS.

BY J. N. BRØNSTED.

Received January 2, 1920

I. Introduction.

The fundamental principles for the treatment of the solubility equilibria in salt solutions have been pointed out in the well known works of van't Hoff and Reicher,¹ W. Nernst² and Arthur A. Noyes.³ By these investigations it has been shown that the important conception of the solubility product is able to represent the solubility phenomena in accordance with the van't Hoff theory of dilute solutions and the Arrhenius theory of the electrolytic dissociation of salts. Indications, however, are found even in these first papers of the fact that the assumption of the constancy of the solubility product, made in the quoted papers and afterwards admitted as a general rule, can account only approximately for the experimental results.

Further investigations by Arrhenius⁴ and by Stieglitz⁵ showed the concentration of the un-ionized portion of the saturating salt was not even approximately constant as required by the theory of solutions, this concentration decreasing rapidly with increasing concentration of another salt having an ion in common with the saturating salt.

Much work on the solubility of salts has since been carried out, of which notably the important investigations of Noyes and his co-workers⁶ deserve special mention. Through this elaborate work experimental results have been obtained corroborating the view of Arrhenius mentioned above, and showing, furthermore, that the solubility product in mixed salt solutions rise considerably with increasing concentration.

To obtain these results the authors apply the method depending on the electric conductance of the solutions, assuming the conductance ratio to be an accurate measure of ionization in pure salt solutions. By introducing the Arrhenius theory of the isohydric solution, and the empirical law which has been found to express the change of the ionization of single salts, an expression is reached which is assumed to govern the equilibria occurring in the mixed saturated solutions.

The results obtained in this way are dependent on the precision of the fundamental assumption, that the conductance ratio is an accurate

¹ *Z. phys. Chem.*, 3, 482 (1889).

² *Ibid.*, 4, 372 (1889).

³ *Ibid.*, 6, 241 (1890).

⁴ *Ibid.*, 31, 224 (1899).

⁵ *THIS JOURNAL*, 30, 946 (1908).

⁶ *Ibid.*, 33, 1643, 1807 (1911).

measure of the degree of dissociation. There has been much discussion respecting the value of this assumption, and we are justified at least in considering it as highly doubtful,¹ since the underlying presupposition that the mobility of the ions is constant is known to be incorrect. Also for other reasons we cannot adopt the conductance method as fitted to account for the constitutions of salt solutions, as will appear from an inspection of the solubility data. It may be stated, for instance, that even when a decrease in the concentration of the un-ionized portion by addition of another salt is to be expected, from the familiar phenomenon known as the "salting out" effect, this decrease as calculated in the cited papers proves to be of quite a different order of magnitude than in the case of a non-electrolyte. Thus a 0.05 *M* potassium nitrate solution, possessing a salting out effect of less than 1% towards non-electrolytes, exhibits an effect more than 30 times as great in the case of undissociated thallic chloride, computed on the basis of the conductance method. Furthermore, a satisfactory explanation of the increasing solubility found in many cases in salts on the addition of other homoionic salts can hardly be afforded by this point of view. Attention is called by Noyes and Bray² to the peculiar behavior of a moderately soluble uni-bivalent salt on addition of a salt with a common bivalent ion. This phenomenon also cannot easily be understood from the standpoint of the ordinary theory. We are justified in consideration of all these discrepancies, in concluding that the conductance method affords no serviceable basis for a theory of solubility. It seems desirable, therefore, to attempt an interpretation of these phenomena from quite a different point of view.

The attempt at a new treatment of the solubility problem contained in the present paper makes no pretence of explaining all the peculiar characteristics of the various solubility curves. It is intended only to show that the multiplicity of types of curves found with hetero- as well as homoionic solvents can be accounted for in a simple way and on a thermodynamic basis by introducing an assumption at any rate approximately true for mixed salt solutions.

Owing to the preliminary nature of this paper an account of the considerable experimental material which has been secured in this laboratory to test the general scope of the new points of view will be postponed for later publication. Only a small number of experiments will be cited in the following sections of this article to elucidate some particularly important conclusions. A more rigorous theoretical treatment of the problem will likewise appear in a subsequent part of this work.

¹ See G. N. Lewis, *THIS JOURNAL*, 34, 1631 (1912); P. Hertz, *Ann. Physik.*, [4] 37, 1 (1912).

² *THIS JOURNAL*, 33, 1643 (1908)

2. Thermodynamic Functions Applicable to Solutions.

The thermodynamic properties of a dissolved substance can be expressed by means of the chemical potential π , this quantity, assuming the validity of the simple gas laws, being given by

$$\pi = RT \ln c + i_c \quad (1)$$

for one mol of the solute, where c is the concentration or number of mols of the solute per liter, and i_c is a constant for the same solvent.

If the gas laws do not hold for the solution, this equation may be replaced by

$$\pi = RT \ln \xi_c + i_c \quad (2)$$

where ξ_c denotes the *activity* of the solute, a conception introduced by G. N. Lewis¹ and conveniently defined by this very equation.

The absolute value of the activity is not determined by (2) and has commonly no significance. It may be established by definition by putting $\xi_c = c$ of the substance in the pure gaseous state at infinite dilution. For our purpose, however, it may be more suitable to put $\xi_c = c$ for the substance at infinite dilution in the solvent used. As a more complete definition of the activity we then have

$$\pi - \pi_\infty = RT \ln \frac{\xi_c}{c_\infty} \quad (3)$$

where π_∞ and c_∞ indicate the chemical potential and the concentration of the substance at infinite dilution in the solvent concerned.

The ratio of the activity to the concentration:

$$\frac{\xi_c}{c} = f \quad (4)$$

is called the *activity coefficient*.² The value of this is constant when Equation 1 holds good, but otherwise varies with varying concentration. When ξ_c is given by (3) the said constant value will be unity.

While the alteration is ξ_c by changing concentration, as seen from Equations 2 and 3, is a merely experimental quantity, no hypothesis whatever being involved in its theoretical determination, the values of the alterations in c , however, will usually depend upon the method employed for its computation. This uncertainty of course also affects the activity coefficient. Different values must be attributed to f , depending on the method employed for the determination of c .

This uncertainty will be removed by introducing for c the stoichiometrically determined concentration of the dissolved substance instead of the "true" concentration. The activity coefficient thereby becomes a thermodynamic quantity like the activity itself. Defined in this way it may be suitably termed the *stoichiometric activity coefficient*.

¹ *Proc. Am. Acad.*, 43, 259 (1907).

² *Noyes and Bray. THIS JOURNAL*, 22, 1626 (1901).

From the nature of Equation 1 it appears that we need not necessarily employ the c -scale to express the concentration in this equation. By substituting x or the mol fraction for c we obtain

$$\pi = RT \ln x + i_x \quad (5)$$

analogous to (1) and

$$\pi = RT \ln \xi_x + i_x \quad (6)$$

analogous to (2). Instead of (3) and (4) we may write

$$\pi - \pi_{\infty} = RT \ln \frac{\xi_x}{x_{\infty}} \quad (7)$$

and

$$\frac{\xi_x}{x} = f. \quad (8)$$

The activities ξ_c and ξ_x are capable of representing the thermodynamic properties of the solution equally well. On dividing by the corresponding concentrations c and x , the same activity coefficient f will result. As in the case of applying the c -scale we have also here to distinguish between the true and the stoichiometric activity coefficient.

An equation of the same significance for dilute solutions as (1) and (5) is arrived at by expressing the chemical potential of the solvent as a function of the concentration. If by π_o and π_{oo} are indicated the chemical potentials of one mol of the solvent at the concentration x and at infinite dilution, respectively, we have for dilute solutions if the gas laws hold good

$$\pi_o - \pi_{oo} = -RT \lambda. \quad (9)$$

The magnitudes of π and x depend on the molal weights M_o and M , attributed to the solvent and the solute, respectively. As to M_o this may, strictly speaking, be chosen arbitrarily but is most conveniently taken as equal to the formula weight of the substance. By fixing M_o we shall find that the value of M is also determined according to Equation 9. The gas laws being valid for the solution means precisely that M , derived in this way from (9), retains a constant value when the concentration changes.

If the gas laws are not valid, (9) must be replaced by

$$\pi_o - \pi_{oo} = -RT \eta_x \quad (10)$$

holding for the solution irrespective of its concentration. η_x may be termed the *osmotic concentration* and is, like ξ , a merely thermodynamic quantity. Putting

$$\frac{\eta_x}{x} = \varphi \quad (11)$$

this ratio called the *osmotic coefficient*¹ proves to be a thermodynamic quantity also when x is the stoichiometric concentration calculated from

¹ Bjerrum, *Z. Elektrochem.*, 24, 321 (1918).

the above values of M and M_0 . Accordingly we have in this case also to distinguish between the true and the stoichiometric coefficient.

Expressing the concentration in the c -scale, (10) and (11) are replaced by the corresponding formulas

$$(\pi_0 - \pi_{00}) \frac{c}{x} = -RT c \quad (12)$$

and

$$(\pi_0 - \pi_{00}) \frac{c}{x} = -RT \eta_c. \quad (13)$$

Furthermore, we obtain

$$\frac{\eta_c}{c} = \varphi. \quad (14)$$

By the equations above a series of functions, ξ_c , ξ_x , η_c , η_x , f and φ are introduced for the purpose of thermodynamic treatment of solutions. Of course, the introduction of these quantities affords no actual progress in the treatment in comparison with the application of the chemical potential or the affinity. All these quantities are correlated thermodynamically and are thermodynamically of the same worth, and only for the sake of convenience or brevity is one of them preferable to another. It will be found, however, as is especially pointed out by Bjerrum,¹ that in the case of dilute salt solutions, which we are to consider in the following, the activity coefficient and the osmotic coefficient will prove to be of peculiar value for the theoretical treatment.

The correlations between the functions introduced may be deduced by means of the fundamental equation of W. Gibbs:

$$x d\pi + d\pi_0 = 0 \quad (15)$$

which holds for dilute solutions; the same equation that in the form

$$x \frac{dA_1}{dx} + (1-x) \frac{dA_2}{dx} = 0$$

has proved of value in affinity determinations. Introducing here (2), (6), (10) and (13), we obtain the equation

$$x d \ln \xi_x = x d \ln \xi_c = d\eta_c = \frac{x}{c} d\eta, \quad (16)$$

which expresses the relation between the activities and the osmotic concentrations.

If more than one substance is present in dilute solution in the solvent, we have to apply the more general formula

$$x_1 d\pi_1 + x_2 d\pi_2 + \dots + d\pi_0 = 0 \quad (17)$$

from which we obtain

$$\left. \begin{aligned} \sum x_i d \ln \xi_{x_i} &= d\eta_x \\ \sum c_i d \ln \xi_{c_i} &= d\eta_c \end{aligned} \right\} \quad (18)$$

¹ *Lec. cit.*

By insertion of (4), (8), (11) and (14), Equation 18 gives us

$$\Sigma x_1 \frac{d \ln f_1}{dx} = x \frac{d\varphi}{dx} - (1 - \varphi) \quad (19)$$

and

$$\Sigma c_1 \frac{d \ln f_1}{dc} = c \frac{d\varphi}{dc} - (1 - \varphi) \quad (20)$$

where

$$\Sigma x_1 = x \text{ and } \Sigma c_1 = c.$$

Putting $x_2 = x_3 = \dots = 0$, Equation 20 is transformed into the equation given by Bjerrum¹ and valid for binary mixtures.

As we are to deal here with solutions containing two or more salts for the purpose of determining the solubility equilibrium, Equations 18-20 may be of special importance.

3. The Theory of the Solubility of Salts in Salt Solutions.

In a saturated solution of a binary salt the chemical potential of the saturating salt must possess a constant value equal to the sum of the chemical potentials of its ions. Denoting by π , π' and π'' the potential of the salt, the cation and the anion, respectively, we have

$$\pi = \pi' + \pi'' = \text{constant} \quad (21)$$

or according to (2)

$$\xi' \xi'' = k \quad (22)$$

which shows the activity product to be constant in a saturated solution. Inserting the activity coefficient by means of (4) we obtain

$$c' c'' f' f'' = k. \quad (23)$$

As in this equation c indicates the molal concentration, f must be the stoichiometric activity coefficient. The alteration of f in the case of addition of another salt must cause the product $c' c''$ — the *stoichiometric solubility product* — also to change with the concentration of the added salt, and this change will depend solely upon the alteration in f . The laws according to which the alteration in f takes place must, therefore, also govern the changing solubility product resulting from the addition of extraneous salts.

We shall now, for the further treatment of the problem, introduce the hypothesis referred to in the introduction. We shall assume that the activity coefficient in a mixed salt solution is the same for any ion of the same type. As will appear from the following, this assumption will markedly simplify the problem before us. Then, since we are only dealing with comparatively sparingly soluble salts, the saturated solution will be either so dilute as to annul, at least approximately, the individual character of any salt, or it will consist nearly completely of the solvent

¹ *Loc. cit.*

alone. It will be possible, therefore, to calculate the activity coefficient by considering only the properties of solutions of single salts.

It is necessary to emphasize, however, the approximative and provisional nature of the above hypothesis. It is introduced here to show only that the general features of the solubility curves may be accounted for on a thermodynamic basis by its means without further assumptions as to the constitution of the solutions, and especially without regard to the degree of dissociation, contingently occurring in the solutions, and hitherto introduced for the treatment of saturated solutions by means of the conductance ratio.

For the calculation of the activity coefficients we can use the results of Noyes and Falk,¹ who have shown that the freezing point data for a number of binary salts can be expressed by the equation

$$2 - i = K\sqrt[3]{c}, \quad (24)$$

where i is the van't Hoff factor, c the equivalent concentration, and K a constant characteristic of each salt. Introducing $2a = K$, (24) may be written

$$\varphi = 1 - a\sqrt[3]{c} \quad (25)$$

from which we obtain, by means of (20) and (17)

$$\log_{10} f = -1.787 a\sqrt[3]{c} = -a\sqrt[3]{c}. \quad (26)$$

If this value be inserted in (23), we have, according to our assumption,

$$\log (c'c'') = 2a\sqrt[3]{c_1} + \text{const.} \quad (27)$$

c_1 denoting the total salt concentration in the saturated solution given by $c_1 = c + s$.

Properly speaking, on the above assumption this relation (27) will hold good only if the solubility is slight when compared with the concentration of the solvent. Since the values of K , as shown by Noyes and Falk, vary only moderately within the range of salts of the same type, and since the presupposition made by assuming the f -values to be equal is only of approximate nature, no essential restriction in the applicability of (27) will result if the requirement above as to the solubility is dispensed with.

In the case of uni-univalent salts the coefficient a as computed from the data of Noyes and Falk proves to oscillate around a value not far from $1/6$. This figure may, therefore, be accepted as an average value and introduced in (27) to express the solubility in this case. If the valences of the ions are higher than unity, a will increase considerably.

From the freezing point data a value for a may be derived which for bi-valent salts is approximately 4 times the a value for uni-univalent salts. This is in concordance with theoretical considerations which render it likely that the a values increase proportionately to the square

¹ *THE JOURNAL*, 32, 1011 (1910)

of the valence. In the case of bi-bivalent and tri-trivalent salts the values $a = \frac{1}{2}$ and $a = 3$, respectively, may be adopted to express the solubility of such salts when introduced in (27).

For the application of this formula we have to distinguish between the cases of the solvent having one ion or none in common with the saturating salt. We may firstly consider the case when a heteroionic solvent is used.

4. Heteroionic Solvents.

In this case c' and c'' in Equation 27 are equal to the solubility or

$$\log s = a\sqrt[n]{c_1} + \text{const.} \quad (28)$$

Introducing here

$$\log s_0 = a\sqrt[n]{s_0} + \text{const.} \quad (29)$$

we obtain

$$\log \frac{s}{s_0} = a(\sqrt[n]{c_1} - \sqrt[n]{s_0}). \quad (30)$$

By means of this relation the solubility ratio s/s_0 can be calculated for varying values of s_0 , c_1 and the coefficient a . The results of this calculation are given in Tables I-III and are represented diagrammatically in Figs. 1 to 5.

In all these diagrams the abscissas represent the molal concentrations of the solvent employed, and the ordinates the solubility ratios s/s_0 . The solubility s_0 being assumed to be negligible in the case represented in Fig. 1, this diagram shows only the influence of the a -value, i. e., the influence of the valence. This influence is seen to be exceedingly marked. While the solubility of an uni-univalent salt is only moderately affected by addition of a tenth molal solvent, the effect in the case of a bi-bivalent one is very considerable, and in the case of a tri-trivalent one enormous.

TABLE I.—THE SOLUBILITY RATIO s/s_0 FOR $a = \frac{1}{2}$.

Heteroionic Solvent.					
c_1	$s_0 = 0$	10^{-4}	10^{-3}	10^{-2}	10^{-1}
0.001	1.080	1.045	1.020	1.006	1.001
0.01	1.180	1.139	1.100	1.045	1.013
0.02	1.232	1.189	1.146	1.078	1.025
0.05	1.327	1.281	1.232	1.148	1.058
0.1	1.428	1.378	1.325	1.228	1.105

TABLE II.—THE SOLUBILITY RATIO s/s_0 FOR $a = \frac{1}{3}$.

Heteroionic Solvent.					
c_1	$s_0 = 0$	10^{-4}	10^{-3}	10^{-2}	10^{-1}
0.001	1.359	1.193	1.081	1.027	1.009
0.01	1.937	1.687	1.471	1.223	1.084
0.02	2.301	2.001	1.733	1.595	1.170
0.05	3.099	2.693	2.319	1.808	1.405
0.1	4.157	3.611	3.104	2.384	1.784

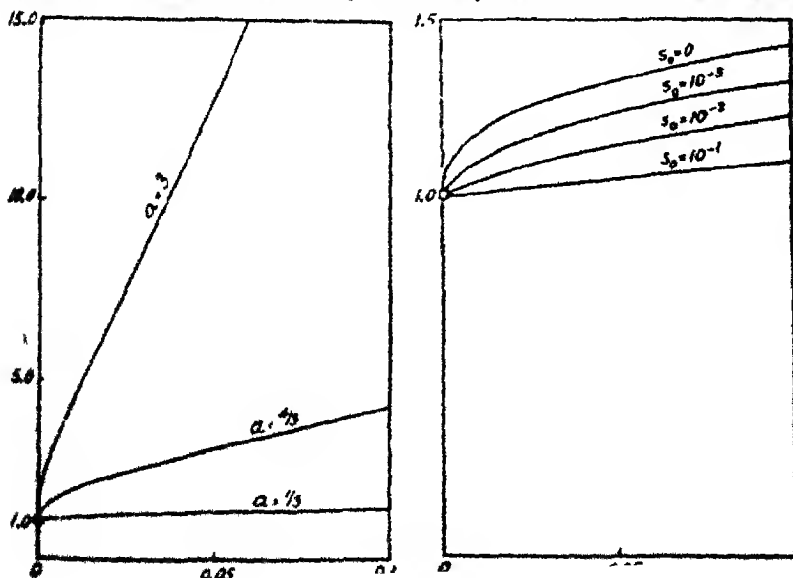
TABLE III.—THE SOLUBILITY RATIO s/s_0 FOR $a = 3$.
Heteroionic Solvent.

c	$s_0 = 0.$	10^{-4}	
0.001	1.995	1.496	
0.01	4.43	3.27	
0.02	6.52	4.80	
0.05	12.74	9.40	
0.1	24.69	18.27	*

$s_0 =$	0.001	c	0.002	c	0.005
0.0008	1.196
0.00337	1.633	0.00227	1.365
0.00778	2.22	0.00629	1.856	0.00320	1.360
0.01673	3.27	0.01454	2.731	0.00999	2.002
0.04361	6.37	0.03933	5.337	0.03045	3.910
0.08762	12.38	0.07932	10.34	0.0621	7.578

$s_0 =$	0.01	c	0.02	c	0.05
0.0053	1.47
0.0107	1.93	0.0038	1.31
0.0160	2.40	0.0074	1.63
0.0213	2.87	0.0110	1.95
0.0267	3.37	0.0142	2.29	0.0015	1.17
0.0310	3.90	0.0172	2.64	0.0025	1.35
0.0358	4.42	0.0198	3.01	0.0030	1.54
0.0443	5.57	0.0243	3.79	0.0031	1.94

The influence of the solubility s_0 is shown in Fig. 2 for uni-univalent salts. The smaller the solubility the more pronounced, obviously, is the



effect of the added salt. The same is seen to be the case when we consider bi-bivalent salts. With the greater solubilities the curves approach straight lines, while the curvature is very marked in the case of slight solubilities.

For tri-trivalent salts the results are plotted in Figs. 3, 4 and 5. It will be observed that the influence of s_0 on the shape and the slope of the curves is similar to that in the foregoing cases only until the solubility $s_0 = 0.02$ molal. At this concentration the effect exhibits a minimum, and at

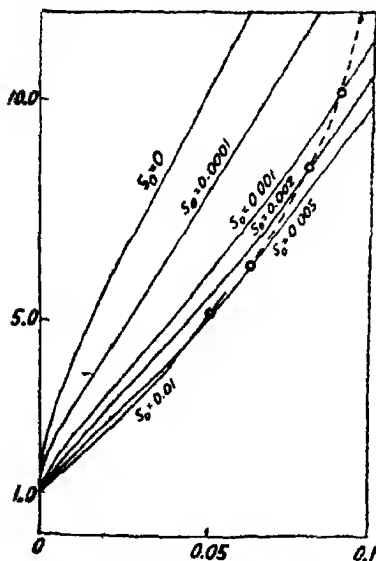


Fig. 3.—Tri-trivalent salts.

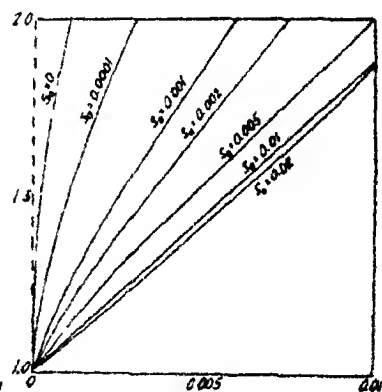


Fig. 4.—Tri-trivalent salts.

higher solubilities the curves rise again showing a curvature in the opposite direction of that otherwise found. In this respect the behavior of tri-trivalent salts diverges widely from that of the salts of lower types, as will especially be evident on considering Fig. 5. The significance of the dotted line in this figure and in Fig. 3 will be mentioned later on.

In a simpler but somewhat less perspicuous way the calculations according to (30) can be represented by employing the total concentration c_t instead of the concentration c of the solvent as abscissas. For this purpose we first transform Equation 30 into the following

$$\log \frac{s_1}{s_2} = a(\sqrt[3]{c_t} - \sqrt[3]{c_h}) \quad (31)$$

s_1 and s_2 representing the solubilities at the total concentrations c_h and c_t , respectively. Putting here $c_h = 0.1$ we obtain the figures given in

For each value of a only one single curve irrespective of the solubility s_0 is obtained. The results are consequently more completely given by this diagram than by the foregoing. On the other hand, it is more difficult to grasp the significance of s_0 by this method.

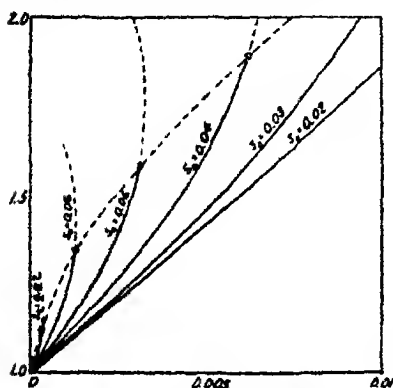


Fig 5 — Tri-trivalent salts

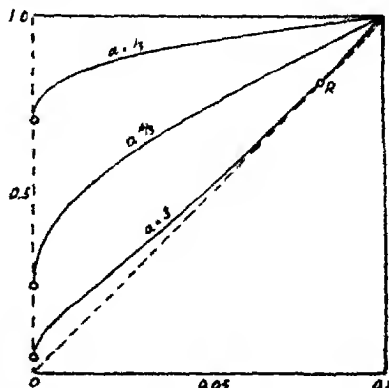


Fig 6

Having now shown the general results furnished by Equations 30 and 31 in the case of heteroionic solvents, we shall turn to their application to some definite examples. In spite of the great amount of experimental work carried out on solubilities partly referred to in the introduction, only a few data are available for the purpose before us. A series of in-

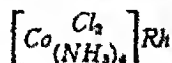
TABLE IV — THE SOLUBILITY RATIO s/s_0 , FOR DIFFERENT VALUES OF a HETEROIONIC SOLVENT

$c + s$	$a = 1/6$	$a = 1/3$	$a = 3$
0.000	0.7003	0.2405	0.0403
0.001	0.7361	0.3269	0.0808
0.002	0.7714	0.3541	0.0967
0.005	0.7984	0.4065	0.1320
0.01	0.8262	0.4660	0.1795
0.02	0.8625	0.5535	0.2642
0.05	0.9291	0.7452	0.5159
0.08			0.7940
0.1	1.0000	1.0000	1.0000

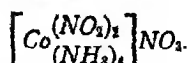
vestigations have, therefore, been initiated in this laboratory for supplying this lack, and an ample experimental material has already been procured, chiefly covering salts of the metal-ammonia type.

From this series, of which a complete account will be rendered in subsequent articles, a few data may be stated in Tables V to IX. The metal-ammonia salts here in question are the following:

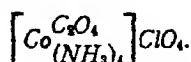
Dichlorotetrammine cobaltic rhodanide or praseo rhodanide



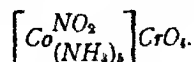
Trans dinitrotetrammine cobaltic nitrate or croceo nitrate



Oxalotetrammine cobaltic perchlorate



Nitropentammine cobaltic chromate or xantho chromate



Further, the data of Noyes and Bray¹ on thallous chloride are shown.

Under $(s/s_0)_{\text{calc}}$ are presented the solubility ratios calculated by means of (30), introducing for a a value such as to make the calculated and the experimental values of s/s_0 agree most closely. It is seen from the tables, first, that agreement can be brought about if we introduce one single a value for any system, second, that these a values for the various systems of uni-univalent salts vary only slightly in the neighborhood of $1/4$. In this respect full concordance exists with the requirements of the freezing point formula. In the case of the bi-bivalent xantho chromate the a value 1.80 must be adopted to represent the experimental data. This value also corresponds to the freezing point measurements and is approximately 4 times as great as in the case of uni-univalent salts.

For tri-trivalent salts no experiments have been carried out with tri-trivalent solvents. The results obtained by employing other solvents, however, show the rise in solubility here to be extremely marked, highly exceeding the effect observed in the case of lower valence. This agrees with the corresponding higher values for a , which may be used in this case.

TABLE V.—THE SOLUBILITY OF PRASEO COBALTIC RHODANIDE IN SODIUM CHLORATE SOLUTIONS AT $t = 0^\circ$, $a = 0.30$

c	s	$(s/s_0)_{\text{calc}}$	$(s/s_0)_{\text{found}}$
0.00	0.00289	1.000	1.000
0.01	0.00306	1.066	1.059
0.03	0.00327	1.132	1.132
0.05	0.00339	1.175	1.173
0.1	0.00360	1.254	1.246

TABLE VI.—THE SOLUBILITY OF CROCEO COBALTIC NITRATE (β -MODIFICATION) IN POTASSIUM FORMATE SOLUTIONS AT $t = 0^\circ$, $a = 0.31$.

c	s	$(s/s_0)_{\text{calc}}$	$(s/s_0)_{\text{found}}$
0.00	0.00494	1.000	1.000
0.02	0.00536	1.092	1.086
0.05	0.005745	1.163	1.164
0.1	0.00621	1.242	1.258

¹ *Loc. cit.*

TABLE VII.—THE SOLUBILITY OF OXALOTETRAMINE COBALTIC PERCHLORATE IN SODIUM FORMATE SOLUTIONS AT $t = 0^\circ$, $a = 0.33$.

c .	s .	(s/s_0) calc.	(s/s_0) found.
0.00	0.00508	1.000	1.000
0.05	0.00597	1.174	1.174
0.10	0.00640	1.258	1.260

TABLE VIII.—THE SOLUBILITY OF THALLOUS CHLORIDE IN POTASSIUM NITRATE SOLUTIONS AT $t = 25^\circ$, $a = 0.355$.

c .	s .	(s/s_0) calc.	(s/s_0) found.
0.00	0.01607	1.000	1.000
0.02	0.01716	1.068	1.068
0.05	0.01826	1.136	1.136
0.1	0.01961	1.217	1.220

TABLE IX.—THE SOLUBILITY OF XANTHO COBALTIC CHROMATE IN MAGNESIUM SULFATE SOLUTIONS AT $t = 0^\circ$, $a = 1.80$.

c .	s .	(s/s_0) calc.	(s/s_0) found.
0.00	0.000258	1.00	1.00
0.02	0.000620	2.39	2.40
0.05	0.000908	3.57	3.52
0.1	0.001237	5.3	4.8

As far as these facts go, the established formulas (30) and (31) may thus be looked upon as able to account for the shape of the solubility curves obtained by varying valence of the ions through the use of heteroionic solvents. As will be observed on closer inquiry into the available experiments, the formulas hold generally only approximately in concordance with the individual behavior which the various salts exhibit in solution, as known also from the individuality in the freezing-point curves.

5. Homoionic Solvents.

In the homoionic solvents the solubility phenomena are much more multifarious than when heteroionic solvents are employed. The correctness of the point of view advanced for the treatment of solubility equilibria will, therefore, be subjected to a more severe test by the employment of solvents of this kind.

From Equation 27

$$\log (c'c'') = 2a\sqrt[3]{c_i} + \text{const.}$$

we obtain by putting $c' = s$ and $c'' = c_i$ and elimination of the constant

$$\log \frac{sc_i}{s_0^3} = 2a(\sqrt[3]{c_i} - \sqrt[3]{s_0}) \quad (32)$$

or

$$\log \frac{s_1c_h}{s_0c_h} = 2a(\sqrt[3]{c_h} - \sqrt[3]{c_0}), \quad (33)$$

where the terms applied have the same meaning as above, and especially the product sc_i indicates the stoichiometric solubility product. By ap-

application of these formulas to the various types of salts the corresponding values of a , given on p. 767, must be introduced.

We shall first consider the effect of the addition of a homoionic solvent qualitatively. To that end Equation 32 is differentiated. Thus we obtain

$$\frac{d \ln s}{d \ln c_i} = \frac{a}{0.6515} \sqrt[3]{c_i} - 1. \quad (34)$$

If c_i be sufficiently small, the first member of the right-hand expression will vanish, and we can write

$$d \ln s = -d \ln c_i$$

In this case the solubility product is constant. The solubility must therefore always decrease by increasing concentration of the homoionic solvent if the solubility in pure water be sufficiently small, and the solvent added in sufficiently slight concentration

From (34) we draw the general inference that the solubility curve must exhibit a minimum when

$$\sqrt[3]{c_i} = \frac{0.6515}{a} \quad (35)$$

showing at smaller concentrations a fall and at higher concentrations a rise with a rise in concentration of the solvent. This minimum lies at very different concentrations according to the different values of a . Putting for a the values adopted above for the various types of salts, we obtain the following figures for the minimum concentration

TABLE X

Type of salt	a	c_{\min}
Uni-univalent	$\frac{1}{2}$	7.5
Bi-bivalent	$\frac{1}{4}$	0.12
Tri-trivalent	3	0.01

In the case of uni-univalent salts the concentration calculated in this way lies far beyond the domain of the established formulas. For salts of higher types, however, the calculated c_{\min} are sufficiently small to render the results reliable. We may, therefore, expect that a minimum in the solubility curve may occur for bi-bivalent and tri-trivalent salts at the total concentration in the neighborhood of 0.1 and 0.01 molal, respectively.

If the solubility in pure water of a bi-bivalent or a tri-trivalent salt exceeds these minimum values 0.1 and 0.01 molal, respectively, the solubility curve must obviously start rising contrarily to the ordinary conception of the influence of a homoionic solvent.

We shall now turn to the numerical calculation of the effect of a homoionic solvent. It is first to be noted that Formula 31 represented in Fig. 6 applies very well also in the case of homoionic solvents when sc_i/s_0 is

inserted for s^2/s_0^2 . In Fig. 6 the curves then represent the square root of the solubility product instead of the solubility itself. A more instructive picture of the correlations in question will, however, be obtained when, as in the foregoing section, the interdependence between the solubility ratio s/s_0 and the concentration of the solvent is represented.

The results of these calculations, according to Equation 32, are given in the following tables, XI, XII, XIII, and the accompanying diagrams:

TABLE XI—THE SOLUBILITY RATIO s/s_0 FOR $\alpha = 1/2$
Homoionic Solvent.

c	s/s_0	c	s/s_0	c	s/s_0
• 0001	0 108	0 1	0 119	0 01455	0 545
0 01	0 01296	0 02	0 0651	0 0475	0 253
0 02	0 00706	0 05	0 0302	0 0999	0 146
• 05	0 00328	0 1	0 0175		
0 1	0 00190				
$s_0 = 10^{-4}$		$s_0 = 10^{-3}$		$s_0 = 10^{-2}$	

TABLE XII—THE SOLUBILITY RATIO s/s_0 FOR $\alpha = 1/3$
Homoionic Solvent

c	s/s_0	c	s/s_0	c	s/s_0
0 001	0 139	0 0098	0 197	0 01295	0 705
0 01	0 0282	0 0199	0 143	0 0445	0 512
0 02	0 0199	0 0499	0 104	0 0954	0 461
0 05	0 0144	0 0999	0 094		
0 1	0 0129				
$s_0 = 10^{-4}$		$s_0 = 10^{-3}$		$s_0 = 10^{-2}$	

TABLE XIII—THE SOLUBILITY RATIO s/s_0 FOR $\alpha = 3$
Homoionic Solvent.

c	s/s_0	c	s/s_0	c	s/s_0
0 00098	0 210	0 00951	0 493	0 0092	1 084
0 01	0 1033	0 0195	0 534	0 0334	1.656
0 02	0 1120	0 0492	0 816	0 0689	3 11
0 05	0 1710	0 0985	1 532		
0 1	0 320				
$s_0 = 10^{-4}$		$s_0 = 10^{-3}$		$s_0 = 10^{-2}$	

We observe from these that Equation 32 underlying the calculations is able to account for the wide diversities which, according to the available data in this field, are characteristic of solubilities in homoionic solvents. With small α -values, that is, with uni-univalent salts the solubility exhibits a pronounced and steady decrease with increasing concentration of the added salt. With medium values of α , that is, with bi-bivalent salts the solubility is likewise diminished, but the fall is less marked than in the foregoing case, and the curves gradually approach a horizontal line. The curves corresponding to a large value of α , or to tri-trivalent salts, finally show pronounced minima and, at higher concentration, a

rapid rise in solubility. In all cases the shape of the curves is markedly influenced by the value of the solubility s_0 in pure water. This value being sufficiently high, we find in the case of a tri-trivalent salt, as mentioned above, that the decreasing portion of the curve will disappear and the curve start rising.

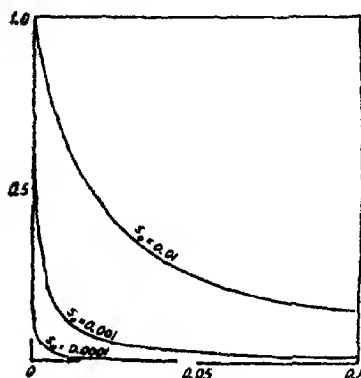


Fig. 7.—Uni-univalent salts.

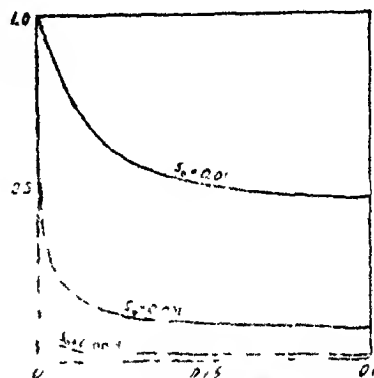
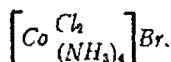


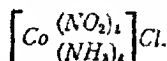
Fig. 8.—Bi-bivalent salts.

A few of the results which have been furnished by the examination of metal-ammonia salts dissolved in homoionic solvents may be stated here for a closer illustration of the applicability of the theory. The salts in question are the following:

Dichlorotetrammine cobaltic bromide or praseo bromide,



Trans-dinitrotetrammine cobaltic chloride or croceo chloride,



Iso-rhodanopentammine cobaltic sulfate,

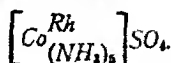


TABLE XIV.—THE SOLUBILITY OF PRASEO BROMIDE IN POTASSIUM BROMIDE SOLUTIONS
AT $t = 0^\circ$, $\alpha = 0.355$

s_0	s_{found}	s_{calc}
0.00	0.00635
0.02	0.00212	0.00212
0.05	0.00107	0.00107
0.1	0.000635	0.000635

TABLE XV.—THE SOLUBILITY OF CROCEO CHLORIDE IN POTASSIUM CHLORIDE SOLUTIONS AT $t = 0^\circ$, $a = 0.38$.

c	s_{found}	$s_{\text{calc.}}$
0.00	0.02216	..
0.02	0.01515	0.01516
0.05	0.01005	0.00991
0.1	0.00640	0.00647

TABLE XVI.—THE SOLUBILITY OF ISO-RHODANOPENTAMMINE COBALTIC SULFATE IN MAGNESIUM SULFATE SOLUTIONS AT $t = 0^\circ$, $a = 1.73$.

c	s_{found}	$s_{\text{calc.}}$
0.00	0.01177	..
0.02	0.01005	0.0096
0.05	0.00980	0.0099
0.1	0.01034	0.0116

TABLE XVII.—THE SOLUBILITY OF THALLOUS CHLORIDE IN POTASSIUM CHLORIDE SOLUTIONS AT $t = 25^\circ$, $a = 0.40$

c	s_{found}	$s_{\text{calc.}}$
0.00	0.01607
0.025	0.00869	0.00873
0.05	0.00590	0.00587
0.1	0.00396	0.00391

The data for these salts and the data of Bray and Winninghoff¹ for thallos chloride are given in Tables XIV to XVII.

The agreement between the calculated values and those found experimentally in all cases proves satisfactory. The values of a to be chosen for producing this agreement are quite concordant with the a values found using heteroionic solvents and by the freezing-point measurements. We observe especially that the a values for the bi-valent salt must again be chosen nearly 4 times as great as for uni-univalent ones. The appearance of a minimum in the curve for the bi-valent salt is likewise in accordance with the theory as mentioned above.

6. The Liquid-Liquid Equilibrium.

Some interesting phenomena whose occurrence may be suspected from the established formulas, such as (30), in the case of polyvalent ions, may

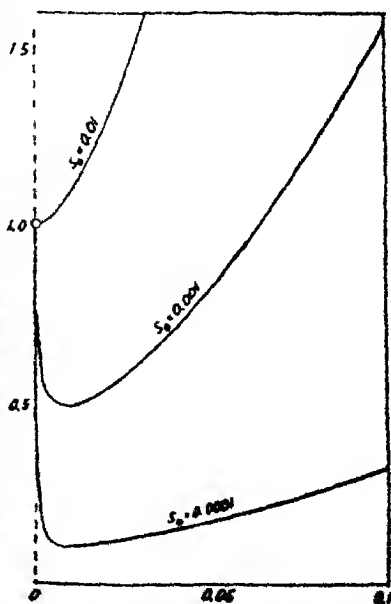


Fig. 9.—Tri-trivalent salts.

¹ *THE JOURNAL*, 23, 1663 (1911).

be mentioned now. As seen from the diagram, Fig. 6, the curvature of the curves for small values of a has the same sign through the whole range of concentrations. As a becomes greater the course of the curves becomes more rectilinear at the higher concentrations and, finally, when a sufficiently large value of a is reached, an inflexion point appears in the curve. Beyond this point the curvature is inverted, and at a certain point (R) the tangent of the curve may pass through the origin.

This case is more clearly represented in Fig. 10 for the addition of a homoionic salt. The solubility s is plotted against the total concentration c_t . The point R corresponds to the point R mentioned in Fig. 6. We have here

$$\frac{ds}{dc_t} = \frac{s}{c_t}$$

or

$$d \ln s = d \ln c_t = d \ln c. \quad (36)$$

Introducing here $s = \xi_1/f$ and $c = \xi_2/f$, ξ_1 and ξ_2 denoting, respectively, the activities of the saturating salt s_1 and the salt s_2 serving as solvent, we obtain

$$d \ln \xi_1 = d \ln \xi_2 \quad (37)$$

or, since $\xi_1 = \text{constant}$ on account of the solution being saturated with s_1

$$d \xi_2 = 0. \quad (38)$$

At concentrations corresponding to the point of contact R the activity of s_2 will thus remain constant with rising concentration.

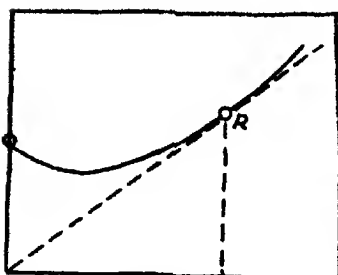


Fig. 10.

While in all stable solutions addition of any substance must cause the potential or activity of this substance to rise we have here arrived at a critical point for the stability of the solution. According to the theory of miscibility of liquids a separation in two liquid layers must take place before this critical concentration is attained.

The situation of this point is determined

by (36). Combining this with (28) we obtain

$$\sqrt[3]{c_R} = \frac{1.303}{a} \quad (39)$$

where c_R indicates the mentioned critical concentration.

According to Equation 18 the point R is also characterized by

$$d\eta = 0,$$

which indicates that the osmotic concentration here shows a maximum. Since this will be the case also in pure salt solutions, the phenomenon of separation here in question must occur in pure salt solutions too.

The same result is easily found by applying Formula 26,

$$\log f = -a\sqrt[3]{c}.$$

Putting here $f = \xi/c$ we have

$$\log \xi = \log c - a\sqrt[3]{c},$$

or, since $d \log \xi = 0$ by $c = c_R$

$$\sqrt[3]{c_R} = \frac{1.303}{a}$$

corresponding to (39).

As a result of these computations we see that the activity of a dissolved salt, increasing with increasing concentration in dilute solution, at higher concentrations will reach a maximum and thereafter decrease. These computations of course have a physical meaning only if the critical point R is reached by solutions which are sufficiently dilute for the applicability of the formulas involved. Introducing in (39) the values of a used above to represent the behavior of the various types of salts, we can calculate the following values of c_R .

TABLE XVIII.

Type of salt.	a	c_R
Uni-univalent. . .	$1/3$	0.59
Bi-bivalent . . .	$2/3$	0.93
Tri-trivalent . . .	3	0.082

Only in the case of tri-trivalent salts, as seen from the figures, does the calculation of c_R afford a trustworthy result, as only in this case is the calculated magnitude of c_R small enough to render the applied formulas at all valid. Even the concentration 0.08 computed for such salts may be regarded as a rough estimation, on account of the deviation from the formulas used increasing rapidly with increasing valence of the ions. We are justified, however, in expecting the separation phenomenon in the case of polyvalent ions at least at fairly small concentrations.

Similarly, the separating layer may be expected to contain a small amount of the solvent. It may naturally be regarded as a salt in liquid state saturated with water under the prevailing conditions. If the melting point of the salt be very low, the liquid-liquid system in certain cases may be a stable one. Usually, however, the equilibrium can exist only because of the insufficient velocity of crystallization, the tendency of the concentrated layer to separate the solid phase being thereby obocured.

According to this view the solubility of salts of higher types may remain far below the solubility of the liquid layer¹ or *a fortiori* far below the critical concentration c_R . In fact, the solubility determinations with such salts, carried out in connection with the above-mentioned investigation on metal ammonia salts, clearly confirms this conclusion, as in all cases solubilities not surpassing 0.001 molar were found.

¹ See J. N. Brønsted, *Z. physik. Chem.*, 56, 683 (1906).

Regarding the separation of a liquid layer from a salt solution, this phenomenon has been realized in a number of cases by admixture of solutions of polyvalent ions of different sign. The separation was in all cases studied by mixing two samples of the solutions concerned under the microscope. Usually the separation occurs instantaneously forming clouds of minute particles gradually uniting to larger liquid drops. The change of the liquid salt into the solid phase usually takes place rapidly. Notably, however, in the case of the trivalent triethylene-diamine cobalt ion the liquid system may be fairly stable, and the procedure of the growth of the drops and their ultimate crystallization furnish a clear illustration of the nature of the phenomenon.

It remains to be said that the phenomenon of the appearance of a salt in liquid state by precipitation is known from other fields of research. The interest of the phenomenon, and its importance for our conception of salt solution, however, makes a closer theoretical and experimental investigation desirable. We shall there have the opportunity of considering the experimental results from this laboratory and from other quarters more closely.

In Figs. 3 and 5 the critical points on the curves are indicated by circles. The dotted line drawn through these points forms the limit of stable solutions. All parts of the curves beyond this limit are dotted in the figures in order to show the unstable or hypothetical character.

Using homoionic solvents a limiting curve of similar significance can be drawn. In all cases the critical points can be determined as points of contact of the tangent passing through the origin.

7. Theoretical Considerations.

Through the results obtained in the foregoing sections we are justified in concluding that the solubility phenomena of salts in solutions of other salts with or without an ion in common may be accounted for on a thermodynamic basis by the simple assumption of the equality of the activity coefficients for salts or ions of the same type in a mixed salt solution.

In particular cases this assumption may prove to hold very exactly, for instance, in mixed solutions of potassium chloride and potassium bromide of slight concentration. Solutions of such a kind will behave in a markedly simple manner at constant total concentration, and may suitably be termed ideal salt solutions. Apart from such solutions, the assumption of the equality of the activity coefficients, as already emphasized in the foregoing, pretends to be only an approximation. It is important to note, however, that the activity coefficients of mixed salts cannot vary independently but, as mentioned in Section 2, are subject to thermodynamic correlations. In a subsequent paper we shall deal with these correlations more thoroughly.

Like our chief assumption concerning the activity coefficient, the cube

root expression employed for $\log f$ is also an approximation. It is clear, therefore, that all the formulas derived in the preceding sections represent only the general shape of the solubility curves, but are not able to explain the peculiar behavior of a particular system. In order to ascertain whether the hypothesis advanced may, properly modified, be able to form the base of a more precise theory of solubility, it must preferably be looked upon in the light of the theory of the complete electrolytic dissociation supported by Bjerrum¹ and Milner.²

In a recent paper³ I have shown that this theory may be applied advantageously in the case of mixed salt solutions to explain the decrease in activity exhibited by a dissolved salt on addition of another salt. From this point of view the increased solubility of salts in heteroionic solvents follows simply from the diminution of the activity coefficient of the ions, no assumption as to the formation of undissociated molecules being involved. In the case of a homoionic addition the solubility product for the same reasons must rise, producing either a rise or a fall in the solubility itself, according to the type of the added salt and the prevailing conditions of the system as a whole.

According to the definite character of the activity in any given solution, the stoichiometric activity coefficient defined in Section 2 and reckoned with throughout this paper, must obviously be equal to the activity coefficient arrived at by the suggestion of complete dissociation, since in this case the actual concentration of the ion is equal to its stoichiometric concentration.

If the calculations carried through by Milner, to determine the influence of the electric charges of the ions, held good for real salts, the activity should be the same in all cases for the same type of salt, and the above approximate hypothesis would then be a rigid law. The deviations manifested by salt solutions, when examined with regard to freezing point or solubility, proves, however, that the ions possess a markedly separate or individual behavior which is appreciable even at fairly small concentrations. From the usual point of view this individuality should be ascribed to diversities in the degree of dissociation. On the basis of the theory of complete dissociation it becomes necessary to attribute to any separate ion a secondary power beside the primary Milner effect which can exert a specific action on ions of the same or of another type. The necessity of introducing such a secondary effect becomes quite natural when we bear in mind that the computations of Milner rest on the presupposition of ideal conditions in the solutions, the ions being considered as charged

¹ *Proc. 7th Intern. Cong. Appl. Chem. (London), 1909. Sec. X, Z. Elektrochem., 24, 321 (1918).*

² *Phil. Mag., [6] 23, 353 (1912); 25, 742 (1913).*

³ *Meddelanden från K. Vetenskapsakademiens Nobelinstitut, 5, No. 25 (1910).*

mass-points, and no regard being paid to the possible hydration of the ions. When the ions are considered as particles of finite sizes, and provided with electrical charges at finite distances from one another, and moreover often combined with a large number of water molecules, they must behave otherwise than the ideal ions which Milner deals with. It is easily understood, therefore, why the theory of Milner is not able to give an exact picture of the behavior of salt solutions.

Considering now the laws of the strong electrolytes as being governed merely by these primary and secondary forces, the interpretation of several solubility phenomena which, according to the ordinary view of such solutions, require particular assumptions for their explanation will appear especially simple. To explain the increasing solubility, which is exhibited by sparingly soluble salts on addition of a homoionic solvent in fairly considerable concentration, we thus commonly suspect the formation of "complex" ions to take place in the solution. Of course in many cases this conclusion may be correct. The solubility of silver cyanide in potassium cyanide, for instance, is undoubtedly due to the formation of a complex silver cyanide ion. The rise in solubility produced in this way is no exceptional phenomenon, however, but generally met with, as mentioned above, when the coefficient α has reached a certain value. From the theory advanced the explanation is given by the double action of the added salt in raising the activity on account of the increasing concentration of the ion concerned, and in causing it to fall on account of the rising electric forces operating between the ions the last mentioned effect exceeding the first in the case of increased solubility. In a solution of hexammine cobaltic sulfate, for instance, we have no reason for believing the ions tend to form complexes. Nevertheless, the solubility of this salt increases rapidly with increasing concentration of a sodium sulfate solution serving as solvent. In this, as in similar cases, the explanation follows as a simple consequence of the electric action which must be associated with the ions according to our theory.

In this connection we may mention a phenomenon to which attention is called by Noyes and Bray.¹ It is stated by these observers that, though in all cases of moderately soluble uni-bivalent salts the solubility is reduced in at least rough conformity with the requirements of the solubility product principle when a salt is added having a univalent ion in common, the decrease of the solubility caused by the addition of an equivalent quantity of a salt with a common bivalent ion does not exceed a few per cent., and the addition of a larger quantity causes the solubility to increase slightly. In other words, the effect on the solubility in the last-mentioned case is on the whole very slight. Harkins² emphasizes

¹ *Loc. cit.*

² *THIS JOURNAL*, 33, 1807 (1911)

this phenomenon as having no resemblance to what would be expected from an application of the solubility product principle.

From our point of view, however, a distinction between the two cases does not exist. Consider a uni-bivalent salt, for instance, lead chloride. Let s_1 and s_2 be the solubility in equivalents in a solution of potassium chloride of the concentration c_1 and in a solution of lead nitrate of the equivalent concentration c_2 . Then we have

$$\frac{s_1}{2} (s_1 + c_1)^2 f_1 f_1'^2 = \frac{s_2 + c_2}{2} s_2^2 f_2 f_2'^2$$

where f_1 , f_1' and f_2 , f_2' indicate the activity coefficients of the lead ion and the chlorine ion in the first and second solution, respectively. Assume the total equivalent concentration to be equal ($= c_t$) in the two cases, and the activity coefficients of the two ions to depend only on the total concentration. The above equation then simplifies to

$$s_1 c_t = s_2^2. \quad (40)$$

This equation shows that a rapid fall in solubility by increasing concentration of an added salt having a univalent ion in common with the saturating salt is easily compatible with the solubility being unaltered by addition of a salt with a common bivalent ion. As in dilute solutions the gas laws approach validity, s_1 will decrease more rapidly in this region, than corresponding to $s_2 = s_1 c_t = k$, and s_2 consequently will not be constant but decrease slightly. At increasing concentrations the fall in s_1 may gradually diminish, corresponding to s_2 passing through a minimum, and thereafter increasing. The effect observed is thus not an abnormal one, but rather in full concordance with what would be expected from the standpoint adopted.

The significance of the valence of the ions is accounted for by assigning according to the type of the salts, different values to the coefficient a in the formulas employed. The relationship between valence and activity coefficient is suggested by Bjerrum¹ and explained through the attracting forces operating between the ions, these forces varying proportionately to the product of the electric charges. No formal derivation of this dependency, however, is given and at the present moment it is not quite decided whether the molal or the equivalent concentration would apply most suitably in the formulas. At any rate, the rapid rise in the electric forces by increasing valence manifests itself very distinctly in the solubility measurements.

As shown in the foregoing, there will be a fall in the activity with increasing concentration if the coefficient a be sufficiently great; that is to say, in the case of tri-trivalent salts. This is easily understood when we consider the solution constituted by ions of high charges. As the concen-

¹ *Z. Elektrochem.*, 24, 321 (1928).

tration increases, the attracting forces between the ions will tend to diminish the activity contrarily to the effect otherwise prevailing in dilute systems, and at a certain point, therefore, the activity will pass through a maximum. This corresponds to the separation of another liquid layer in equilibrium with the solution, as mentioned above. This phenomenon is quite similar to the break in continuity produced by the compression of a gas beyond the saturation point, the cohesive forces between the molecules here replacing the electric forces operating between the ions. As the incomplete miscibility of liquids according to the theory of Hildebrand¹ is sensibly dependent upon the difference in internal pressure of the liquids concerned, we must suggest the supercooled liquid salts of high valence to be in possession of extremely high internal pressure, as is exactly to be expected from the conception of the salts being, in the solid and the liquid state, also more or less completely dissociated. At any rate the assumption of a decreasing dissociation of the salts with increasing concentration may not be able to account for the separation phenomenon appearing in very dilute solutions in a similarly simple way.

Finally, we may consider briefly some other fields in which the theory supposedly may be advantageously applied. It is clear that the effect which is here assumed to increase the solubility of a salt by addition of other salts, must exist also in the case of unsaturated solutions and may be able to alter the equilibrium occurring in homogeneous solutions as a whole.

Consider first the electrolytic dissociation of the solvent itself. In accordance with the above view an addition of salt to pure water must diminish the activity coefficient of the hydrogen and the hydroxyl ion. As on the other hand, the potential of the water suffers no perceptible alteration on small additions of salt, a rise in the dissociation of the water must ensue. The "dissociation constant" is thus actually no constant, but increases with the concentration of the solute, say a uni-univalent salt, in the same way as the solubility product of a correspondingly soluble salt. If by k we denote the dissociation product in pure water, the value of the product of the two ions at varying concentration of an added uni-univalent salt, calculated by means of (27) may be expressed approximately by the following figures:

TABLE XIX.—THE DISSOCIATION PRODUCT OF WATER IN SALT SOLUTIONS OF THE CONCENTRATION c .

c	$[H^+][OH^-]$
0	k
0.001	1.17
0.01	1.39
0.02	1.51
0.05	1.77
0.1	2.05

¹ THIS JOURNAL, 38, 1452 (1916).

The alteration in the dissociation product is thus very considerable. In a tenth molar solution it is about twice the value in pure water. That such a change has not been observed hitherto is due to the fact that usually only the activity of the ions, and not their true concentrations, are available for the experiment. If the activity coefficient be altered to the same degree for the two ions, the effect must then be obscured.¹

As in the case of water, we shall find an effect of the same kind with other weak electrolytes. We may establish quite generally the fact that any equilibrium in aqueous solution involving incompletely dissociated electrolytes may be influenced correspondingly by addition of salts. By consideration of such cases, however, the phenomenon known as the "sailing out" effect must be not disregarded. This effect will cause the activity of a non-electrolyte, or of the undissociated portion of a weak electrolyte, to increase with increasing salt concentration. The solubility of a slightly soluble weak acid, for instance, will for these reasons exhibit a maximum at a certain salt concentration at which the Milner effect is compensated by the "salting out" effect. Experiments of Hoffmann and Langbeck² with weak acids have given results which confirm this view.

For the treatment of the solubility phenomena of the strong electrolytes the results obtained with non-electrolytes or weak electrolytes, however, are of wide consequence. For it may be surmised that the "salting out" effect is not restricted to uncharged molecules alone but is present in the case of widely dissociating salts also. It is very probable that the "secondary effect" mentioned in the previous sections as being peculiar to the individual salts, respecting their solvent power, may be found to be in close connection with the salting out effect. As an illustration may be noted that potassium hydroxide, showing the most pronounced salting out effect upon non-electrolytes, also reduces the solubility of salts much more markedly than other solvents examined in this respect.³ This fact has caused A. E. Hill⁴ to surmise without paying attention to the exceptional character of the substance used that the solubility generally diminishes on addition of heteroionic solvents.

Having now in the present paper advanced the general points of view

¹ If the H^+ and the OH^- ions are hydrated to a different extent, increasing concentration of an added substance must alter the dissociation equilibrium of water in favor of the anhydride of the most hydrated ion. This fact being appreciable in strong solutions makes it possible to explain a divergence of such solutions from the neutral state, as indicated by electrometric measurements. Possibly the results of Palmer and Melander (*Z. Elektrochem.*, 21, 418 (1915)) are to be interpreted in this way.

² Hoffmann and Langbeck, *Z. physik. Chem.*, 51, 385 (1905).

³ J. N. Brynsted, Meddelanden fr. K. Vetenskapsakademiens Nobelinstitut, 5, No. 25 (1919).

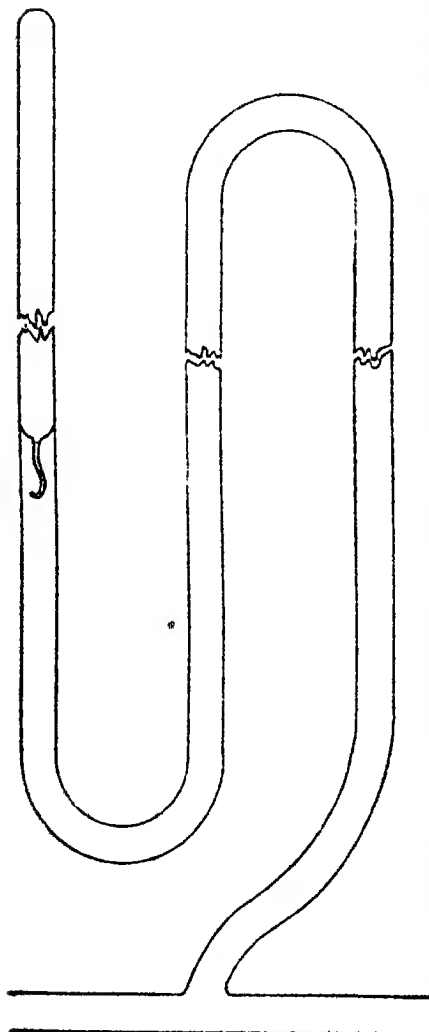
⁴ A. E. Hill, *This Journal*, 32, 1186 (1910).

NOTE.

from which the solubility equilibrium in salt solutions supposedly ought to be considered, we may in subsequent articles turn to a more detailed treatment of the whole problem in connection with the publication of the remaining part of the experimental results.

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NOTE.



Manometer for Vacuum Distillation.—The form of manometer commonly employed in vacuum distillations suffers from two principal disadvantages, the first consisting in the danger of air or moisture being carried into the vacuous space by the repeated movements of the mercury with change of pressure; the second, which is the more serious, consisting in the liability of the sealed end of the manometer tube to be broken by the impact of the mercury on suddenly readmitting atmospheric pressure into the apparatus.

Both of these defects may be eliminated by the use of a hook-shaped trap such as is commonly employed on accurate barometers. This trap effectually prevents the passage of air into the vacuous space, and if the capillary of which the hook consists be sufficiently fine as to retard the movement of the mercury, the danger of breaking the tube is effectually prevented.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, HARVARD UNIVERSITY.]
ON THE CHEMICAL MECHANISM OF ORGANIC REARRANGEMENTS.

BY ARTHUR MICHAEL.

Received November 4, 1919.

In a later paper on "Ring Formation and the Strain Theory," the analogy between the course of rearrangements in cyclic and acyclic derivatives will be discussed from the affinity-energy-spatial relations of the atoms, and, as a wide discrepancy is found in chemical theory in regard to the cause and the mechanism of such changes, it seemed desirable for a correct understanding of the correlation to consider beforehand the subject of rearrangement from the same point of view.

In a homogeneous chemical system, an intramolecular rearrangement takes place through a change in the positions of certain atoms or groups of atoms in the molecule, and the new, isomeric product may belong to the same, or to a different chemical type; in the latter case the process may be called a *type rearrangement*. When the isomerization takes place intermolecularly, it proceeds with the dissociation of the substance into simpler parts, which then unite to form a compound that is more stable under the conditions of the experiment.

In a heterogeneous chemical system, the change in the chemical structure may occur with the loss of a component part of the substance, through the catalytic influence or the chemical action of the energy in the reagent, with isomerization of the residual structure. Or, by the union of the substance with the reagent, when, owing to the chemical energy thus added, an isomerization in the substance part of the "polymolecule" takes place with partial conversion of its free energy into bound energy and heat, and is followed by the breaking down of the system into the isomerized substance and the reagent. Reactions of this class are always type rearrangements.

The factors that determine an intramolecular rearrangement are: first, the extent of the free chemical energy at the interchanging atoms or groups of atoms; second, their affinity for each other and for the atoms in the group to which they migrate; third, the amount of energy required to separate the migrating parts from the remaining atoms of the group, which constitutes a hindrance to the arrangement, and, finally, the heats of formation of the isomerides or the two products. As these factors may now be connected with the chemical structures of organic substances, an analysis of the changes from this standpoint is an explanation of the rearrangement.

The conversion of iso- into tert.-butyl bromide is an excellent illustration of direct isomerization, and of the subtle relations that may determine stability towards heat energy. In the methinyl group of the iso-

derivative the affinity between the carbon and hydrogen has been greatly decreased by the numerous, adjacent hydrogen atoms,¹ and, as the tert. bromide has a greater heat of formation, the affinity and energy relations exist in the primary bromide for a facile, direct isomerization. What is considered an unusually pure preparation of isobutyl bromide is stable considerably above its boiling point, but this stability is due to the presence of an anticatalyte in infinitesimal quantity, as the purest product obtainable changes slowly into the tertiary compound at room temperature and rapidly far below the point of ebullition.²

The historic conversion of ammonium isocyanate into urea is an admirable example of isomerization through dissociation. All ammonium salts are broken down by heat energy more or less readily into ammonia and acid, and, whether the isocyanic acid (HOCN) thus set free keeps its structure under these conditions or is converted into the less acidic, intramolecularly better neutralized carbonimide (OCNH), is immaterial to the final phase of the reaction, as each of the forms is capable of adding ammonia; in the latter case forming directly carbonamide, and, in the former, an enol isomer which will pass over into that product.³

Although the chemical system is heterogeneous at the start, it is not infrequent that the actual rearrangement takes place in a homogeneous system. This may occur through the increment of chemical energy to the rearranging molecule by the formation of a "polymolecule" (catalytic rearrangement), by that of a real addition product of the substance and the reagent, or by the replacement of one or more of the atoms in the substance by other atoms or groups of atoms, whose affinity and energy relations favor the change. Thus, phenylhydroxylamine is a weak base, and, although the energy required to separate the hydroxyl group and a hydrogen of the aromatic nucleus from the respective groups is not very considerable, the free energy in the hydroxyl group is not large nor can there be a decided difference between the heats of formation of the substance and the isomeric aminophenol. Increasing the free energy, and decreasing the hindrance to an isomerization by the increment of heat energy, results in the intermolecular breakdown into aniline, azo- and azoxy-benzene and water. With the formation of acid phenylhydroxylamine sulfate, however, all the energy and affinity factors change favorably toward an intramolecular rearrangement. The weak base is now strongly overneutralized, and the product with its large surplusage of negative chemical energy not only works towards converting the weak basic component of the salt into a stronger base, whereby more of the excess of its free negative energy will be converted into bound energy and

¹ Michael, *THIS JOURNAL*, 32, 997 (1910).

² Michael and collaborators *Ann.*, 379, 263 (1910); 393, 81 (1912); *THIS JOURNAL*, 38, 653 (1916).

³ Michael *J. prakt. Chem.* [2] 60, 411 (1890).

heat, but the affinity of the negative hydroxyl group for a hydrogen of the aromatic nucleus has been increased, and the energy necessary to separate them out of the groups in which they are placed has been greatly decreased. *With the formation of acid aminophenol sulfate¹ a considerable entropy increase must, therefore, take place; indeed, it is an invariable rule in the intramolecular rearrangements of all acidic and metallic organic derivatives, that the changes occurring in the structure of the mother substances are of a nature to neutralize the surplus of free energy existing in the salts.² And, it is an unfailing characteristic in all such molecular reconstructions that they proceed with an increase in the entropy of the system; that is, by a greater conversion of the free into bound energy and heat than the opposite energetic changes.*

One of the primary conditions for intramolecular rearrangement without dissociation is the accumulation of free energy in considerable amount at one of the atoms or group of atoms in the molecule. Thus, while phenylhydroxylamine decomposes readily at 100° into various products and water, phenylchloroamine or phenylnitramine, in which the weakly negative hydroxyl group is replaced by the strongly negative chlorine atom, or nitro group, with the aid of the greater amount of unneutralized, free chemical negative energy in them, are readily transformed into the intramolecularly much better neutralized, chloro- and nitro-aniline.

The Amide → Amine Rearrangement.

Hofmann³ showed that the bromoamides are converted into isocyanates on treatment with silver carbonate, and Tiemann⁴ first suggested that the latter are intermediate products in the Hofmann amine synthesis, a view which was proven experimentally by Mauguin.⁵ Tiemann⁴ also indicated

¹ The further analysis of this rearrangement will appear in a paper on the structure and properties of benzene and its derivatives.

² The most casual examination of this subject in chemical literature and in textbooks, will suffice to show that these conditions cannot be too strongly emphasized. It will be noticed, that rearrangements are frequently assumed to take place with substances that are in themselves either perfectly stable, or, when heated sufficiently, decompose in an entirely different manner. It is certainly remarkable that so many typical rearrangements should still be theoretically misinterpreted in this way, as, for instance, with the transformation, at a high temperature, of methylaniline-iodo- and chlorohydrate into the corresponding salts of *o*-, and *p*-toluidine, respectively. In this case, the so self-evident explanation has been known for many years (Michael, *Ber.*, 14, 2107 (1881)) *i. e.*, that the isomerization must take place through the dissociation of the salts into aniline and the methyl halide. They can now only react differently on each other, as they cannot reunite under the prevailing conditions of temperature, the halogen atoms attacking the easily replaceable hydrogen in the aromatic nucleus of the base, with the formation of salts of the more strongly basic toluidines.

³ *Ber.*, 15, 412 (1882).

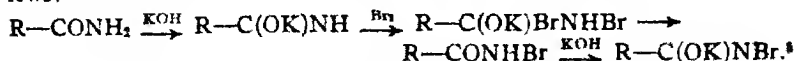
⁴ *Ibid.*, 24, 4163 (1891).

⁵ *Compt. rend.*, 149, 790 (1909); *Ann. chim.*, [8] 22, 310 (1911).

⁶ *Ber.*, 15, 4164 (1891).

that the antecedent step in this reaction, and the formation of aniline through the isocyanate in the distillation of benzo-hydroxamic acid, consisted in the formation of the unstable structures $RC(O)N$. This now very generally accepted interpretation was developed and extended to other similar reactions by Stieglitz,¹ who ascribed the rearrangement to "the free or latent valences at the nitrogen atom," and later,² in agreement with Jones,³ to a shifting of electrons from carbon to nitrogen.

Hantzsch⁴ has given experimental evidence in favor of enol structures for the potassium acyl bromo-amides, which are probably formed as follows:



¹ *Am. Chem. J.*, 18, 751 (1896), 29, 49 (1903). The literature on the subject, and a discussion of other interpretations of the rearrangement, may be found in these papers.

² *THIS JOURNAL*, 36, 288 (1914); 38, 2047 (1916).

³ *Am. Chem. J.*, 50, 441 (1913).

⁴ *Ber.*, 35, 252 (1902). See also Stieglitz, *Am. Chem. J.*, 29, 49 (1903).

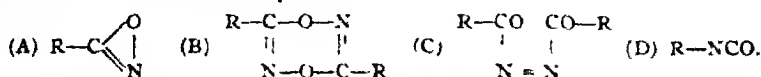
⁵ Schroeter (*Ber.*, 42, 2337, footnote 4 (1909)) believes that the formula $R-CONKBr$ is equally well established, since it is impossible to decide which of the desmotropic forms, $R-C(OH)NBr$ and $R-CONHBr$, is the more acidic, and the hydrogen of "ammonia residues" may have "strongly acidic character," *e. g.*, in hydrazoic acid. The latter statement appears somewhat exaggerated, as the affinity constant of the acid at 0° is only $1 \cdot 10^{-4}$ (Hantzsch, *Ber.*, 32, 3066 (1899)). Although the fundamental principles governing the structural rearrangements that may take place with the conversion of neutral organic substances into metallic derivatives were fully developed in 1887 (Michael, *J. prakt. Chem.*, [2] 37, 473 (1888); *Am. Chem. J.*, 10, 158 (1888); 14, 481 (1892)), there seems to be still some uncertainty on the relation of such changes to the chemical composition and the structure of the substances.

An accumulation of negative energy must result when a number of nitrogen atoms are grouped together, as in hydrazoic acid, but the strength of its acidic manifestation depends also on a second factor, *viz.*, that the negative energy at the nitrogen group is largely in a free state. It is this condition of the negative energy that gives that acid its chemical resiliency towards positive chemical energy; if the free energy at the 3 nitrogen atoms had been converted into bound energy in forming the group, to the extent that takes place in forming the nitrogen molecule (*THIS JOURNAL*, 32, 990 (1910)), it might act almost neutral towards water, or even towards weak bases.

The quantity of negative energy in the oxygen of benzoamide is not only greater than that of the nitrogen, but also its quality towards that in the potassium atom, and a relatively larger proportion of it is in a free, chemically more potential, condition. The action of potassium on benzoamide can take place, therefore, only at the oxygen atom; in driving out a hydrogen and forming at once $C_6H_5-C(ONa)NH$, the maximum entropy of the system is attained, and no further structural change can occur under the experimental conditions (*ibid.*, 1902).

Even Hantzsch (*Ber.*, 35, 229 (1902)), who has contributed experimentally so much to confirm the writer's views, has not fully understood the subject, for he believes that in an organic product sodium always joins on to oxygen in preference to nitrogen, and, for that reason, sodium cyanoacetic ester has the structure $NC-CH=C(ONa)OR$. The nitrogen in a nitrile group is always rich in free energy, and the quality

The affinity-energy-spatial relations of the metal and halogen in these derivatives are extremely favorable for interaction, for the mother-substances are not very acidic¹ and, therefore, in each of these atoms there must be still considerable free chemical energy of an opposite character; besides, the affinity of bromine for nitrogen is only slight, and the metallic and halogen atoms are in the spatially closest possible positions (1,5). With the elimination of potassium bromide a structural change must take place, for there is an enormous amount of free negative energy at the nitrogen and oxygen atoms of the residual structure $\text{CH}_3\text{—C(O)N}$, and, as they are both in direct union with carbon, they have greatly reduced the affinity between the carbon atoms. A chemical reconstruction in 6 directions² is now possible



The second law of thermodynamics demands that in the spontaneous chemical change that follows the primary phase, the free energy in the unstable structure shall pass over to the maximum possible extent into bound energy and heat; the chemical limitations to the realization of this goal are, the affinity relations between the atoms, and the energetic hindrances to a transformation. The formation of (A)³ involves the considerable in cyanoacetic ester for sodium has been increased through the negative influence of the oxygen atoms. On the other hand, when the hydrogen of a carboxyl group is replaced by alkyl, the negative energy of the oxygens is neutralized to a more or less considerable extent, and it is primarily the free energy that is converted. The magnitude of this loss of negative energy in the esterification of the carboxyl group is shown by the incapacity of benzylacetic ester to form a *merotropic* sodium derivative and the greater *chemical potential* (*Ann.*, 363, 21 (1908)) in the CN than in the COOEt group for sodium, that such a product may be obtained from benzonitrile. That a greater neutralization of negative energy occurs by the union of the metal to the nitrogen of cyanomacetic ester is also evident from the fact that the compound is decidedly more acidic than malonic ester (see *Am. Chem. J.*, 43, 358 (1910)).

It would certainly add to clearness in chemical terminology in this field and to precision in the theoretical conceptions, if the suggestion (Michael, *Ann.*, 363, 30 (1908)) were adopted, that the terms tautomerism, or desmotropy, be used only to designate the capability of certain substances to exist in, and to pass over intramolecularly into forms with different chemical structures, and *merotropy* to that of substances passing over into a derivative of a desmotropic form, through the combined influence of the affinity-energy relations in a heterogeneous chemical system. The phenomena are closely related, but not necessarily coincident (*ibid.*, 31-35).

¹ Hantzsch, *loc. cit.*, states that the salt reacts alkaline towards litmus, but may be titrated with alkali by using phenolphthalein

² The very improbable intermediate formation of $\text{CH}_3\text{—O—NH}$ is not taken into consideration. See Hesse, *Am. Chem. J.*, 29, 56 (1903). The affinity-energy conditions exist for the formation of R—O—CN , but the entropy increase in that case would be much less than with that of R—NCO .

³ Hantzsch, *Ber.*, 27, 1256 (1894). Stiehlitz, *Am. Chem. J.*, 20, 65 (1898).

expenditure of energy to shift the segmentations of the oxygen and nitrogen spheres on the carbon sphere,¹ to the large extent necessary for forming the 3-membered ring derivative, which can be effected only by the free energy at the nitrogen and oxygen atoms. The change in this direction is debarred, however, for the affinity between these elements is too slight for them to perform so large a work. It is remarkable, therefore, that such a cyclic arrangement not only exists in *phenyl-cyclo-nitrile oxide*,² but it is formed in a closely allied reaction, *viz.*, in the spontaneous decomposition of sodium benzohydroxamic chloride, $C_6H_5C(NONa)Cl$.³ The energy-spatial relations of the metal and halogen in that product are strictly comparable to those of the similar elements in the potassium acylbromoamides, and the outward analogy between the two decompositions is so striking that Wieland⁴ investigated the problem whether such cyclic nitrile oxides are not the primary intermediate products in the Hofmann amine reaction. Although the phenyl derivative is partially converted by heat energy into the isocyanate, the interpretation had to be given up, as the substance could not be prepared from benzobromoamide, nor is aniline formed in its decompositions.

Why do two structurally and energetically so similar classes of compounds as $RC(NONa)Cl$ and $RC(OK)NBr$ give so entirely different products of decomposition? With the replacement of the hydroxyl-hydrogens in a hydroxamic chloride and enol bromoamide by a metal, a considerable transformation of its free energy and that in the halogens into bound energy takes place through space, which must result in these atoms being brought closer together spatially. This change evidently carries with it an approachment of the elements joined directly to the metal and halogen, that is, their segmentations on the respective carbon atoms are brought nearer together; a spatial juxtaposition that increases when the halogen and metal enter into direct union, and pass out of the

¹ Michael, *THIS JOURNAL*, 40, 705 (1918)

² The usual names, phenylnitrile oxide, and also benzonitrile-N-oxide (Richter's "Lexikon," 1910-11, 344), are chemically ambiguous. Besides cyclo, the prefix *epi* may be used to designate ring formation, as it is already connected in chemical nomenclature with such a structural condition; for instance, epichlorohydrin. Votocék (*Ber.*, 44, 360 (1911)) has suggested prefixing *epi* to distinguish diastereomeric derivatives, and to designate the appearance of such products as *epimerism*. Although this suggestion was adopted in Meyer-Jacobson's "Lehrbuch" (I¹, 912), it cannot be considered an apt addition to chemical terminology, since *epi*, as stated above, is already connected with an entirely different chemical relationship, and there is absolutely no connection between the derivation of the prefix and its use to characterize *diastereomerism*. The latter term is far superior to *epimerism*, and, instead of *epi*, it would be better to prefix *diastereo-* or *disallo-*, *e. g.*, glucose and diastereo- or disallo-glucose.

³ Werner, *Ber.*, 27, 2199 (1894); Wieland, *ibid.*, 40, 418, 1667 (1907); 42, 803, (1908).

⁴ *Ibid.*, 42, 4207 (1909); see also Schroeter, *ibid.*, 42, 2339 (1909).

system as a salt. The quantity of the free energy at the Δ -C and Δ -O, respectively the Δ -N and Δ -O, obviously now becomes very considerable, but the capability of these atoms to overcome the hindrance to form a 3-membered ring, evidently depends also on the quality. The affinity of carbon for oxygen is highly developed, while that of nitrogen for oxygen is correspondingly slight, and, in this contrast in the affinity values of the end Δ -atoms of the intermediate structures, is to be found the striking difference in the following phases of the reactions ¹

Formula B represents a more stable structure, in whose formation an entropy increment over that by (A) would ensue, as the energetic hindrance to the development of its 6-membered ring is smaller than that in the tricyclic arrangement in (A). The chemical obstacle is, however, the slight affinity between the nitrogen and oxygen atoms. It is again an affinity relationship that prevents the realization of (C), as the direct union of the negative acyl radical with the nitrogen has so materially diminished the attraction between nitrogen and nitrogen that such a structure could show but a very slight stability towards heat energy. Moreover, the free energy content of (C) would be quite large; considerably greater than that of (B), and probably only slightly less than that of (A). All the energetic relations in the unstable complex favor rearrangement according to the Tiemann-Stieglitz interpretation, which finds its expression in (D). In the first place, the hindrance to the migration of the *hydrocarbyl*² group is slight, as the affinity between the carbon atoms has been greatly decreased by the direct negative influences of both the oxygen and the nitrogen atom, while, on the other hand, that of the nitrogen for the hydrocarbon group, is decreased comparatively much less, as the influence of the oxygen is only indirect. That the affinity between *hydrocarbyl* and nitrogen in isocyanates is decidedly developed is evident from the properties of the substances, for in none of their chemical decompositions does the rupture occur at that point. Finally, in regard to conversion of the

¹ When an organic compound contains atoms that may interact on each other, an intramolecular decomposition is favored if these atoms are spatially near to each other, or, if the atoms joined directly to them are in the same steric relationship (Michael, *J. prakt. Chem.*, [2] 60, 335 (1899)). In the first case, the question of a monomolecular ring formation depends more on the affinity relations of the atoms that become momentarily unsaturated than in the second, as they are farther apart spatially, and the energetic hindrance is therefore greater. Sodium chloroacetate does not give a tricyclic derivative, because the carbonyl group reduces the affinity between the methylene carbon and the natrioxyl oxygen so much that they are not able to overcome the energetic hindrance, but replacing the carbonyl by the methylene group, i. e., sodium ethylene chlorohydrate, increases these affinity relations sufficiently to lead intramolecularly to the cyclic ethylene oxide.

² This word is suggested as a generic name for any monovalent hydrocarbon radical, irrespective whether it is saturated or unsaturated. *Hydrocarbene* and *hydrocarbins* might be used to express collectively ethylenic and acetylenic hydrocarbon derivatives.

free energy in the unstable system, there can be no doubt that it is greater in the formation of (D) than it would be in that of (A) and (C), and probably there is only a small difference between it and that of (B).

Rearrangements in Aliphatic α,β -Glycols.

In no other class of organic rearrangements are the chemical changes more complicated and dependent on chemical structure than those accompanying the loss of water in the α,β -glycols. The theoretical interpretation of this subject is difficult or impossible from the current theoretical views, and it offers an excellent test of the applicability of the affinity-energy-spatial view-point to a very intricate problem in organic theory.

Under ordinary conditions, glycol must have a fumaroid configuration,¹ which is the spatial form favoring the intramolecular elimination of water,² when only one of the hydroxyl groups is involved in the process. Simultaneously with such a dehydration, either a gyration of the methylene radical on the common carbon axis, or a migration of the hydrogen of the hydroxyl to the place occupied before by the abstracted hydroxyl, must take place.³

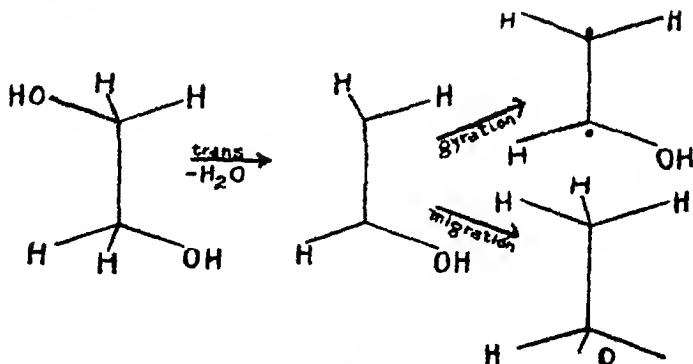


Fig 1.

These changes require each the expenditure of a certain amount of the free energy in the unstable, intermediate configuration, and that of the

¹ Michael, *THIS JOURNAL*, 40, 707 (1918). The reasons there stated for the fumaroid stereostructures of monobasic acids apply to all saturated organic substances.

² Michael, *J. prakt. Chem.*, [2] 52, 359 (1895).

³ The absence of an atomic symbol always implies a carbon atom. Unsaturation is shown by one or two points over or below the atoms (Michael, *J. prakt. Chem.*, [2] 46, 204, 222-254 (1892)), and the shorter lines between unsaturated than between saturated atoms denotes that the centers of the atoms in the unsaturated group are nearer together than those in the corresponding saturated group (Michael, *THIS JOURNAL*, 40, 706 (1918)).

ogy to the stereomeric, dibasic acids, should take place through the maleinoid configuration:¹

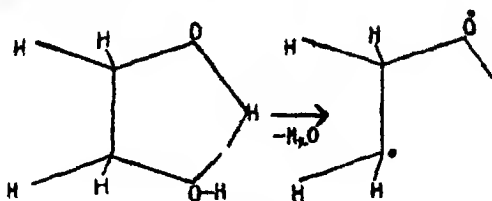


Fig. 2.

In this case, too, an unstable structure is formed, which may pass over, through migration of a hydrogen atom, into aldehyde; polymerize, through the union of two systems, to diethylene oxide, or directly form ethylene oxide.

The glycols, in which one to three of the nuclear hydrogen atoms are replaced by hydrocarbyl radicals, may lose water according to (A) and (B), but Type A is structurally prevented with the total replacement of these hydrogens. In the presence of an alkyl group, (R), a third type of elimination (C) becomes possible, and the intermediate structure thus formed may rearrange, by trans-migrations² of R and the hydroxyl-hydrogen, into a ketone:

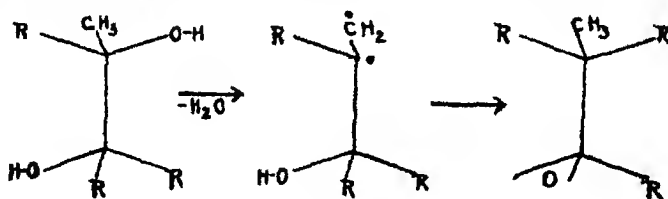


Fig. 3

which is able to isomerize the oxide, whereas PbCl_2 and AgCl are without action upon it.

Markownikoff (Liebig's *Jahresber.*, 55, 785 (1902); *J. Chem. Soc.*, 84, 200 (1903)) appears to have suggested views somewhat similar to those of Krassusky, but as his paper, too, appeared only in Russian, it is impossible to form an intelligent opinion on them, and on the "principle of chemical equilibrium," from the résumés in non-Russian journals.

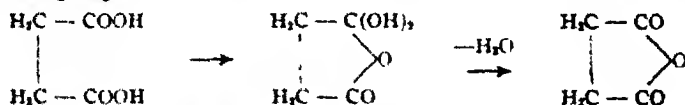
¹ This projection of the sphere configuration of glycol, and those of other substances in the paper, were obtained by connecting the centers of atomic spheres in direct union by straight lines, and extending the lines, when the spatial juxtapositions of certain atoms are to be accentuated, to the points on the surfaces that are nearest together in space. The actual spatial relations of the atoms are more accurately and clearly represented in this way than in the skeleton configurations now in use.

² The facility of the pinacol rearrangement indicates that the hindrance to transmigration is slight; perhaps, like in the trans-addition and trans-elimination of the halogens and the halhydric acids (*THIS JOURNAL*, 40, 1690 (1918)), less than that

The rearrangements with the fatty α,β -glycols take place with the use of more or less *dilute* solutions of strong acids, which cannot possess that direct, considerable affinity for water essential for the procedure according to (B). Whether the decomposition of the mono-, di-, and tri-substituted glycols proceed according to (C) or to that of (A) depends on whether more energy is required to remove the separate hydrogen atom used in the formation of the water from an alkyl radical than from the axial carbon in the carbinol group. As the influence of the hydroxyl diminishes the affinity between carbon and hydrogen more than that of an alkyl group, Type A represents the process in all but the fully substituted α,β -glycols. This relation has been demonstrated experimentally by the course of the rearrangements in the *sec*-*tert*-glycols; for instance, the decomposition of methyl diethyl glycol might take place according to Type C, and yield methyl diethyl aldehyde, but it actually takes place according to (A), and gives methyl isopropyl ketone.¹ And, it is also proven by the behavior of unsym. dimethyl glycol, on heating with the dehydrating mixture of acetic anhydride and sodium acetate, when the in-

occurring in the corresponding *cis*-process. There appears to be no doubt that ring-formation takes place through the *cis*-configuration, but the question may be raised whether, when it occurs with the loss of a component part of the substance, it is a direct process between the *cis* groups, or a *trans*-elimination with a practically simultaneous rearrangement?

Thus, instead of succinic anhydride being formed from *cis*-succinic acid through the following stages



its formation may be expressed, stereostructurally, by

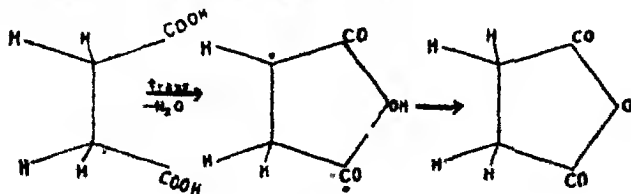


Fig. 4.

In this interpretation the long-standing conflict between the stereochemical conception of ring-formation, and the experimentally established addition-elimination relations, is avoided (*ibid.*, 1706). It may be mentioned that a third interpretation is possible, *viz.*, the dehydration proceeds through the formation of succinic mono-ketene, $\text{HOOC} - \text{CH}_2 - \text{CH} = \text{CO}$. Anhydrides are easily formed intermolecularly from ketenes and acids, and with the very favorable energy-spatial relations of the interacting groups in the ketene-acid, a spontaneous transformation into succinic anhydride would undoubtedly follow its formation.

¹ Tiffeneau and Dorencourt, *Ann. chim.*, [8] 16, 237 (1909).

intermediate dimethyl vinyl alcohol becomes stabilized through the formation of the acetate; but the carbinol isomerizes to dimethyl acetic aldehyde when it is set free by saponification.¹

The role of the acids in these rearrangements is evidently catalytic, that is, the first phase is the formation of a "polymolecule,"² of carbinol and acid. Recent investigations³ have made it probable that certain atoms, or groups of atoms, in a molecule show a selective affinity, even for solvents,⁴ and, from this point of view, a "polymolecule" should be considered as possessing an intermolecular structure.⁵ For instance, the relatively basic hydroxyl group is that component part of glycol, which should show the greatest affinity for an acid, and in their "polymolecule" the molecule of the acid should be grouped on that of the glycol, so that the acid radical is spatially as near as possible to one or to both of the hydroxyl groups.⁶

The catalytic properties of acids in these rearrangements may now be explained. In the formation of the "polymolecules" comparatively little of the free energy in the acid and the carbinol is lost, and that in the new system, which will perform the work involved in the ensuing chemical processes, is very much greater than that in the glycol alone. Further, the negative energy of the acid decreases the affinity of carbon for hydrogen,⁷ which facilitates the elimination of water, and which may be an important factor in determining the decomposition of these glycols according to Type A, as the carbon of the carbinol group should be spatially nearer to the acid than that in an alkyl group.

The stability of these "polymolecules" towards water should stand in a direct relation to the relative positivity of the alkyl radicals in the glycol. Therefore, with one of these groups remaining the same, it should increase in changing the other alkyl radical from primary to secondary, and then to tertiary.⁸ According to these relations, the strength, and the concentration, of the acid necessary for catalysis should decrease with

¹ Tiffeneau, *Compt. rend.*, 150, 1118 (1910).

² Michael, *Ber.*, 34, 4028 (1901); 39, 2140, 2570; *Am. Chem. J.*, 39, 3 (1909); 41, 120 (1911), *THIS JOURNAL*, 32, 991 (1910), 40, 1696, 1702 (1918).

³ Langmuir, *Met. Chem. Eng.*, 15, 469 (1916); *THIS JOURNAL*, 38, 222 (1916); 39, 1848 (1917), Harkins, *ibid.*, 39, 354, 541 (1917).

⁴ The writer believes that the formation of "polymolecules" of solute and solvent plays an important role in the interesting phenomena described in the researches of Harkins (*loc. cit.*) on "The Structure of the Surfaces of Liquids." See Michael, *J. prakt. Chem.*, [2] 60, 429 (1899).

⁵ Michael, *THIS JOURNAL*, 40, 1702, footnote (1918).

⁶ In the "polymolecule" of substituted glycols and sulfuric acid, which is the acid generally used in the rearrangements, the oxygens of the sulfonyl radical should be grouped spatially as near as possible to the hydroxyls of the glycols.

⁷ Michael, *THIS JOURNAL*, 32, 996 (1910).

⁸ Michael, *J. prakt. Chem.*, [2] 60, 432 (1899).

increasing positivity of the alkyl groups, which appears to be the rule. And, in the direction of increasing the reaction facility, should be also the same relative relation in the alkyl radicals, since the affinity of the attached carbon for a nuclear hydrogen is decreased proportionately, while that of such hydrogens for the hydroxyl of the other carbinol group is correspondingly increased.

The course of the elimination of water from the mono- and di-alkyl α,β -glycols, in relation to their structure, may be followed from the "addition-elimination" law,¹ and the "principle of partition."² In agreement with the law, a tertiary carbinol loses water much more readily than a secondary of the same series, and that derivative easier than the primary.³ Linnemann⁴ found that propylene glycol may be heated with water in a sealed tube to 215°, without undergoing a change, but the addition of only a trace of hydrochloric acid to the mixture causes the formation of aldehyde. This behavior, which is so excellent a proof that the decomposition is catalytic in its mechanism, shows how much easier the secondary carbinol group parts with its hydroxyl than the primary group. According to the partition principle, however, the difference between the direct and indirect influence of methyl and hydrogen should not suffice to throw this elimination process entirely in one direction, and acetone in a small proportion should also be formed, which agrees with Eltekoff's⁵ result, while Flawitzky,⁶ like Linnemann, failed to detect its formation. Flawitzky,⁷ however, obtained apparently considerable methylisopropyl ketone, besides isovaleric aldehyde, in the decomposition of isopropyl glycol. This result agrees with the theory; in methyl glycol the 3 methyl hydrogens are in the unimportant fourth position to the carbon of the primary carbinol group, while, in the isopropyl derivative, there are 6 hydrogens in the very important 5 position,⁸ which should give that carbinol group relatively a more secondary character than methyl does the primary radical in propylene glycol. For this reason, in the decomposition of a monoalkyl glycol, the proportion of ketone to aldehyde should increase with the relative positivity of the alkyl group, but in amount the yield of ketone should always be much less than that of aldehyde. According to the "principle of partition,"⁹

¹ Michael, *Ber.*, 34, 4221 (1901)

² Michael, *THIS JOURNAL*, 32, 1006 (1910)

³ Michael and Zeidler, *Ann.*, 385, 227 (1911).

⁴ *Ann.*, 192, 63 (1878). Krassusky, *Bull. soc. chim.*, [3] 24, 873 (1900), found that a number of fatty glycols could be heated with water to 240° without change.

⁵ *Ber.*, 11, 990 (1878)

⁶ *Bull. soc. chim.*, [2] 30, 535 (1878)

⁷ *Ber.*, 10, 2240 (1877); 11, 992 (1878).

⁸ See "scale of combined influence," *THIS JOURNAL*, 32, 999 (1910); 34, 849 (1912); 40, 707, 717 (1918); 41, 308 (1919).

the sym. dialkyl glycols with different alkyl radicals should yield mixtures of two isomeric ketones, and, with the increasing difference between the relative positivity of the two groups, the proportion of that ketone, in which the more positive alkyl is directly joined to the carbonyl group, should increase in a direct relation to the polarity divergence of the hydrocarbon radicals.¹ Thus, theoretically sym. methyl ethyl glycol should yield a mixture of methyl propyl and diethyl ketones, and sym. methyl propyl glycol the methyl butyl and ethyl propyl derivatives, in which the first and third products should be in somewhat greater proportion. And, the relative difference in their amounts should be slightly larger in the ketones of the higher carbon series.

Pinacol \rightarrow Pinacolone² Rearrangement in the Fatty Series.

In the tetra-alkyl glycols, the process according to (A) is structurally debarred, and the mechanism of the remarkable type rearrangement to ketones, has been the subject of an extended discussion. The first explanation was given by Erlenmeyer, senior,³ who assumed the elimination of water to proceed with the formation of an unstable hydroxy-cyclopropane derivative, and that the ketone is then formed through the migration of the hydroxyl-hydrogen to the methylene-carbon, with the opening of the ring. The formation of intermediate ring derivatives was applied to explain other, similar rearrangements, and was investigated experimentally by Montagne,⁴ who found that *p*-tetrachlorophenyl-pinacol yields a *pinacolone* with all the chlorine atoms still in *para* positions, whereas one of them should be in the *meta* position, if the reaction proceeds through a 4-membered ring compound. Montagne concluded that a pinacol rearrangement never takes place through the formation of an intermediate ring product, but such a comprehensive conclusion is hardly warranted by his experimental results. Erlenmeyer's hypothesis applied to wholly aromatic pinacols would lead to the intermediate formation of products with stable, 4-membered carbon rings, whose properties would preclude a transformation into a *pinacolone* under the experimental conditions. On

¹ See *J. prakt. Chem.*, [2] 60, 432 (1899) for the polarity grouping of the alkyl radicals. The subject merits a quantitative investigation, in which the semicarbazide method (*THIS JOURNAL*, 41, 396 (1919)) may be used.

² It seems inconsistent to modify the group names of certain classes of organic compounds to conform better with their chemical structures, and leave chemically unsuitable names of other classes unchanged. For this reason, *pinacolone* is used instead of pinacoline.

³ *Ber.*, 14, 322 (1881). See, also, Coururier, *Ann. chim.*, [6] 26, 438 (1897); Nef, *Ann.*, 318, 37 (1901); Zelinsky and Zelikow, *Ber.*, 34, 3251 (1901); Lindner, *Monatsh.*, 32, 403 (1911).

⁴ *Rec. trav. chim.*, 21, 30 (1902); 24, 105 (1905); 25, 379, 411 (1906). The result was confirmed by similar experiments of Acree (*Am. Chem. J.*, 33, 120 (1905)) and by those of Meerwein (*Ann.*, 396, 210 (1913)).

the other hand, the trimethylene ring, assumed by Erlenmeyer to explain the changes with fatty pinacols, would certainly be easily ruptured between the methylene and carbinol groups, and this phase of his explanation is feasible from a chemical point of view, and a pinacolone would then be formed.

Thoerner and Zincke¹ observed the formation of aryl ethylene oxides in the decomposition of tetraphenyl and diphenyl-ditolyl pinacols by dilute acids, and that such products may be transformed into the corresponding *pinacolones* by the same reagents that serve for the first reactions. On the basis of these observations, Breuer and Zincke,² who had found analogous results with the hydrobenzoin, assumed the formation of substituted ethylene oxides, or less probably that of the diethylene oxides, as the primary phases in the transformations to ketones. Montague³ called attention to the much greater stability of the oxides than the pinacols towards the employed reagents, and expressed the opinion that definite intermediate products are not formed, but that the rearrangements occur simultaneously with the elimination of water. And, he found an experimental support to this view in Meerburg's⁴ results with tetrachlorobenzopinacol and the corresponding oxide, where the reactions are of the first order, and where the transformation into *pinacolone* proceeds faster with the first compound. An extended study of the rearrangements of the α,β -glycols, and those of the corresponding aromatic iodohydrals, led Tiffeneau⁵ to the conclusion that they are usually preceded by a phase of "desorganisation," with the formation of structurally unstable complexes, which reorganize to stable products, owing to the tendency of free valences to neutralize each other. According to this, quite generally accepted, view, the rearrangement of pinacol leads first to the formation of $(\text{CH}_3)_2 = \text{C} - \text{C} - (\text{CH}_3)_2$, which may change not only into *pinacolone*,



through the migration of a methyl group, but, also, by the direct polymerization of two groups, into tetramethyl diethylene oxide. Somewhat later, Faworsky⁶ showed that on heating ethylene glycol with a small proportion of conc. sulfuric acid, diethylene oxide distills off as the main product of the reaction, and that when this product is heated with the concentrated acid it gives aldehyde. He concluded, therefore, that the formation of the latter substance from glycol goes through that of di-

¹ *Ber.*, 11, 68 (1878). Also, Klinger and Lounes, *ibid.*, 29, 2158 (1896).

² *Ann.*, 198, 148 (1879). Erlenmeyer, Jr., *ibid.*, 316, 84 (1901); Nef, *ibid.*, 335, 243 (1904).

³ *Rec. trav. chim.*, 24, 105 (1905).

⁴ *Ibid.*, 24, 131 (1905).

⁵ *Rev. gén. Sci.*, 18, 589 (1907), *Bull. soc. chim.*, [4] 1, 1221 (1907).

⁶ *Chem. Centr.*, 1907, I, 1112.

ethylene oxide. Influenced by these results, Tiffeneau¹ abandoned his previous hypothesis, and assumed that dialkylene oxides are the intermediate products in these rearrangements. These theoretical conclusions are characteristic of the tendency to base explanations on rigidly mechanical conceptions of valence, and to generalize from results obtained from a single group of substances, irrespective of the fact that different affinity-energy and spatial relations may appear in other, although analogously structured groups; also, of the indifference toward taking the known correlations into consideration that exist between the main chemical processes and the structures of organic substances.²

The conclusions drawn by Montagne from Meerburg's results are too general. It is permissible to conclude from the greater reaction velocity of tetrachloro-benzopinacol compared to that of the oxide with acetyl chloride, that the transformation in this case does not proceed through the oxide, but not to extend the conclusion to all pinacol rearrangements, even in the aromatic series. For instance, phenyltolyl pinacol in alcoholic solution, and in the presence of a very small amount of hydrochloric acid, passes over into the oxide at room temperature, and the *pinacolone* formation under these conditions should proceed through that of the oxide.³ Further, it is not safe to conclude from the transformation of tetrachloro-benzopinacol being a reaction of the first order, that the relation is true for all rearrangements involving the migration of an aryl group. For instance, although benzopinacol gives a monomeric product of dehydration, the stereomeric hydrobenzoinz yield dimeric products, and both the oxides are convertible into *pinacolones*.

A comparison of the reagents and the conditions for aromatic and aliphatic pinacols shows that, with one or two exceptions in the first group, the facility of rearrangement in the two series differs considerably. With the aromatic compounds, strong dehydrating agents at moderate temperatures, or concentrated solutions of strong mineral acids at higher temperatures, are required, while with the fatty substances the changes take place readily with very dil. sulfuric acid; pinacol itself rearranges even with a 5% solution of oxalic acid at 100°.⁴ As such dilute solutions cannot be dehydrating in the sense of a direct affinity for water, Tiffeneau's first interpretation, which implies the existence of a strong dehydrating capacity in the reagent, is manifestly in variance with the conditions prevailing with the fatty pinacols.

¹ *Bull. soc. chim.*, [4] 1, 1226 (1907). See Meerwein, *Ann.*, 396, 215, footnote (1913).

² Michael, *J. prakt. Chem.*, [2] 60, 287, 409 (1899).

³ Meerwein, *Ann.*, 396, 212 (1913), showed that the oxide is not the intermediate derivative in the case of diphenyl-diphenylene glycol, and concluded that this relation holds in all pinacol rearrangements.

⁴ Vorländer, *Ber.*, 30, 2366 (1897).

And, the later view is not tenable for the following reasons. Faworsky distilled glycol with a small amount (4%) of conc. sulfuric acid, which leads first to the formation of the acid sulfate. This energetic substance is formed in the presence of a large excess of glycol, and reacts upon it; not intramolecularly, because the alcoholic group in unchanged glycol is relatively much more basic than that in the acid sulfate, and the formation of a 3-membered ring derivative would involve a strong energetic hindrance. The second phase leads, therefore, to the formation of diethylene glycol, which condenses intramolecularly to the volatile, hexacyclic diethylene oxide. The latter compound has the property of uniting with strong sulfuric acid to form an "oxonium" salt or a "poly-molecule," which on heating will strive towards conversion as far as possible into volatile products. As the stability of the hexacyclic ring has been greatly decreased through the superabundant negative energy in the added acid component, and, for the same reason, also the affinity between the hydrogens and the carbons in the methylene groups, at a temperature below the dissociation point into acid and oxide, a migration of two hydrogen atoms to adjacent methylene groups, with the rupture of the ring, takes place, and, with the volatilization of the low boiling aldehyde and the regeneration of the acid, the maximum entropy of the system under the experimental conditions is realized. Faworsky's idea, that the glycols in their conversion with loss of water into carbonyl derivatives are first changed into dialkylene oxides is founded on a misconstruction of the sulfuric acid reaction, and it is untenable for the reason that the rearrangements occur under conditions (*i. e.*, heating the pinacols with slightly acidulated water) where the formation of oxides are not only precluded, but the reverse reactions would take place. And, further, because under the conditions where glycol yields diethylene oxide, *i. e.*, distillation with strong sulfuric acid in a small proportion, pinacol gives 2,3-dimethylbutadiene almost quantitatively, and pinacolone in small amount only.¹

In the previous explanations of the rearrangements in fatty pinacols, that characteristic property of tertiary carbinols to dissociate easily, through the catalytic influence of very dilute mineral acids, into alkynes and water² has not been taken into consideration. That pinacol, which contains two tertiary carbinol groups, undergoes such a dehydration under the conditions of the rearrangement is shown by the simultaneous formation of 2,3-dimethylbutadiene, and that small yields of ketones from aliphatic pinacols are accompanied by the formation of such hydrocarbons in

¹ Bayer and Co., *Chem. Centr.*, 1912, II. 1757.

² Butlerow, *Ann.*, 144, 22 (1867); 189, 75 (1877); Michael and Zeidler, *ibid.*, 325, 228 (1911).

larger proportion.¹ Indeed, the butadiene is formed almost quantitatively in the distillation of pinacol with traces of salts that react acidic.²

The elimination phase in the pinacol rearrangement proceeds, therefore, according to Type C,³ and leads in the first step to the formation of dimethyl-isopropenyl carbinol,⁴ which has the requisite affinity and energy relation in its atoms to isomerize, with the aid of the energy in the catalytic reagent, into *pinacolone*, and with the conversion of its free energy into bound energy and heat to a very considerable extent.⁵ For, the Δ -hydrocarbon group of the carbinol has a large content of free energy, then, the hydroxyl-hydrogen and the methylene-carbon atoms are in the spatially close 1,5-position, which means a slight resistance to the migration of the hydrogen, and, finally, the affinity of the carbinol-carbon atom to a directly joined methyl group has been considerably lessened through the influence of many hydrogen atoms in important positions.⁶

¹ Meerwein, *Ann.*, 396, 227 (1913)

² Bayer and Co., *Chem. Centr.*, 1912, II, 1854

³ See page 796.

⁴ This alcohol was first prepared by Choupotsky and Mariutza (*J. Chem. Soc. Abs.*, 48, 727 (1890)) by heating the monochloro derivative obtained in the addition of chlorine to tetramethyl-ethylene with water. The reaction evidently proceeds first with the formation of tetramethyl-ethylenedichloride, which shows the characteristic property of the tert. halides in splitting of halhydric acid very readily. The monochloro alkene is, therefore, dimethyl-isopropenyl-methyl chloride, and not chloro-tetramethylethylene, as it is called. The corresponding carbinol was also obtained by Courtot (*Bull. soc. chim.*, [3] 35, 969 (1896)) in the treatment of α -2- β -trimethyl- β , γ -dibromo-butyric acid with potassium carbonate in a freezing mixture. To explain this remarkable rearrangement, leading under such mild conditions to the formation of a tertiary carbinol from a primary, and a secondary, bromo derivative, Courtot (*ibid.*, 659) assumes shifting in the positions of the bromine atom and the carboxyl group, and compares the migration of COONa to that of COOE, in the forced abstraction of water by P₂O₅ from ethyl phenylhydroxypivalate (Blaise and Courtot, *Compt. rend.*, 141, 724 (1905)). The rearrangement is followed by the elimination of CO₂ and HBr to form dimethyl-isopropenyl-methyl bromide. The writer can find no analogy between the two reactions (see page 820), and believes that the first step in the rearrangement lies in the interaction of β -bromine and sodium, with the consequent loss of CO₂, to form $\text{CH}_2\text{Br}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)_2$, which, by addition of water, passes over into $\text{CH}_2\text{Br}-\text{CH}(\text{CH}_3)-\text{COH}(\text{CH}_3)_2$, and then into dimethyl-isopropenyl carbinol by the loss of HBr.

⁵ *Pinacolone* represents an intramolecularly extremely well neutralized structure (Michael, *THIS JOURNAL*, 32, 1004 (1910)), which accounts for its large heat of formation (Zoubuff, *Chem. Centr.*, 1899, I, 516).

⁶ Michael, *THIS JOURNAL*, 32, 997 (1910). How readily a methyl migration may take place is well shown by the formation of sym. tetramethyl-ethylene on warming tert.-butyl-methyl bromide with alcoholic soda (Tissier, *Ann. chim. phys.*, [6] 29, 362 (1893)). The affinity of the alkali for hydrobromic acid suffices in this rearrangement because that of carbon for carbon in the tertiary group, and of carbon for hydrogen in the primary group, has been greatly diminished through the influence of the many, specially near, hydrogen atoms. The rearrangement is favored by the formation of that transition state in which the migrating methyl group is partially bonded to both the carbon atoms of the tetramethyl-ethylene system.

The rearrangement may be represented by

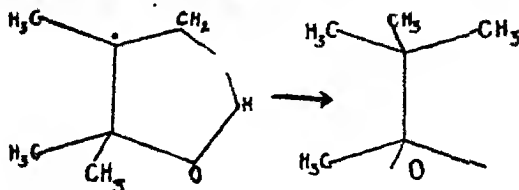


Fig. 5

No better proof can be advanced for the correctness of this interpretation than that the dimethylbutadiene is converted into *pinacolone*¹ when heated with dil. sulfuric acid, since the first step in that process must consist in the addition of a molecule of water, with formation of the Δ -carbinol.²

Nonexistence of the Pinacol \rightarrow β -Oxide Rearrangement.

At the suggestion of Lieben,³ Kohn⁴ and Samec⁵ examined the behavior of tetra-ethyl glycol, and Zumpfe⁶ the corresponding propyl derivative, towards dilute sulfuric acid. Along with the corresponding Δ -hydrocarbons, products of monodehydration were obtained, which failed to show some characteristic properties of ketones, *i. e.*, they did not react with hydroxylamine or with zinc ethyl. Lieben⁶ concluded from these properties that radicals larger than methyl are unable to migrate, and that, instead of *pinacolones*, β -alkylene oxides are formed by the intramolecular addition of the hydroxyl groups in the intermediate isoalkylenyl dialkyl carbinols to the Δ -carbon atoms.

forces are most symmetrically distributed and which, therefore, according to the "thermochemical law of structure" (*ibid.*, 1904), must have the largest heat of formation of the isomers. A thermochemical investigation of the alkynes, and of other unsaturated groups of derivatives, from this point of view would be of great theoretical importance.

¹ Coururier, *Ann chim phys*, [6] 26, 493 (1892).

² Mariutza (*J Chem Soc. Abs.*, 58, 728 (1890)) heated this carbinol with dil. sulfuric acid (1%) to 100°, and obtained a product boiling above 100°, which he believed to be a polymerization product of the dimethyl butadiene. The product undoubtedly consisted largely of *pinacolone* (106°), as any isomer of the simplest possible polymer, C_8H_{16} , would show a very much higher boiling point. Interesting is the formation of the butadiene from the Δ -carbinol when very dilute acid (0.1%) is used, which is a characteristic property of tertiary carbinols (Michael and Zeidler, *Ann.*, 385, 227 (1911)). A systematic investigation of the relations between the concentration of the acids (see Michael and Brunel, *Am Chem. J.*, 41, 118 (1909); 42, 267 (1912)), and the nature of solvents (Michael and Zeidler, *loc. cit.*) to the character and course of the reactions and to the structure of the organic substances, should yield theoretically interesting results.

³ *Monatsh.*, 26, 37 (1905).

⁴ *Ibid.*, 111.

⁵ *Ibid.*, 28, 738 (1907).

The first conclusion has been shown to be erroneous; indeed, Meerwein¹ found that ethyl instead of methyl migrates in the *pinacolisation* of unsym. dimethyl-diethylglycol, and Parry² that propyl and isoamyl in preference to methyl in the corresponding mixed glycols. According to the theory of the pinacol rearrangement developed in this paper, the main factors deciding the course of the transformation in the above-named glycols are: first, the relative ease of the elimination of a molecule of water from the tert. carbinol groups of different series; second, the relations in the amount of energy required to separate the migrating alkyl group, and, third, the heats of formation of the isomeric ketones that may be formed in the structural change.

It is unfortunate that the relations of the first-named factor to structure have not been determined experimentally, but they may be deduced theoretically by the application of the "addition-elimination law,"³ which, as yet, is without an exception, and, according to which, in a series of homologous, isomeric or stereomeric compounds, the substance which is formed easier by addition from a corresponding Δ -derivative, will lose the addenda the more readily. Isobutene has been found by experiment⁴ to add water, under the influence of dilute acids, more readily than any other isoalkene, and tert butyl alcohol should lose water, therefore, more easily than any of the homologous tert. carbinols. The second of the above factors is determined by the influence of hydrogen atoms in loosening the affinity of carbon to carbon, and this influence should grow in passing from methyl to ethyl and from that radical to propyl.⁵ Finally, according to the "thermochemical law of structure,"⁶ that ketone among the two isomers that may be formed, will have the larger heat of formation, in which the positive alkyl radicals are to the greater extent under the influence of the negative carbonyl group. In glycols of the type $(\text{CH}_3)_2\text{—COH—COH}(\text{C}_n\text{H}_{2n+1})_2$, in which n is 2 or a larger number, the elimination of water should take place, therefore, more readily from the dimethyl carbinol side of the pinacol. Further, the influence of the hydrogen atoms in loosening the affinity of carbon to carbon is greater in the larger alkyl radicals. And, finally, of the two isomeric *pinacolones* that may be formed, $\text{CH}_3\text{—CO—C}(\text{C}_n\text{H}_{2n+1})_2\text{CH}_3$ and $\text{C}_n\text{H}_{2n+1}\text{—CO—C}(\text{CH}_3)_2\text{C}_n\text{H}_{2n+1}$, it is apparent that the positive atomic forces are grouped more symmetrically towards the negative carbonyl nucleus in the latter substances, which

¹ *Ann.*, 396, 222 (1913); also, Romburgh and Wensnik, *C. A.*, 8, 3297 (1914).

² *J. Chem. Soc.*, 107, 108 (1915).

³ Michael, *J. prakt. Chem.*, [2] 52, 289 (1895); 60, 373 (1899); *Ber.*, 34, 4216 (1901); *This Journal*, 40, 1690 (1918).

⁴ Michael and Brunel, *Am. Chem. J.*, 41, 128 (1909); 48, 268 (1912); Michael and Zeidler, *Ann.*, 385, 239 (1911).

⁵ See *This Journal*, 34, 850 (1912); 40, 708 (1918); 41, 398 (1918).

⁶ Michael, *This Journal*, 32, 1004 (1910).

should have, therefore, the larger heat of formation. In ketones of the above type, therefore, all the principal energy factors coincide to favor the migration of the larger alkyl radical,¹ and the theory explains the experimental results.

In view of this relationship, it seems remarkable that derivatives of the type $(C_nH_{2n+1})_2COH - COH(C_nH_{2n+1})_2$, in which n is larger than 1 and bilaterally of the same value, should give β -oxides and not *pinacolones*. Against the formation of the oxide class of compounds, it may be urged that the formation of 1,3-oxides by intramolecular addition would involve the very considerable expenditure of free energy necessary to overcome the hindrance to the formation of the 4-membered ring derivative, and that there is no experimental precedence to support such an interpretation. Further, that the supposed β oxides are stable towards water at 200°, which is a very improbable property for a ring derivative with its affinity relations and its content in free energy. The small reactivity or indifference of ketones with the above structures towards hydroxylamine can no longer be considered crucial evidence of the absence of the keto-carbonyl group; not only are aliphatic ketones now known that are indifferent towards the reagent, but, if the products of rearrangement are keto derivatives, their slight reactivity would agree with their structures.² The same chemical inertia should be shown by them towards zinc ethyl, as in each case it depends on the reduction of the affinity relations, and the free energy, in the carbonyl group, by the bilateral, spatial action of large alkyl groups.³

The oxidation of the supposed oxide from tetraethyl glycol was carefully studied by Samec,⁴ who identified diethyl-acetoacetic acid, asym. diethyl acetone, diethyl glycolic and diethyl-acetic acids, and isolated besides an acid, $C_{10}H_{20}O_{11}$, of unknown structure, among the products formed. This chemist, although he called attention to the correlation of these products of oxidation to a *pinacolone* constitution of the supposed oxide,⁵ endeavored to explain their formation from the latter point of view,⁶ but on the basis of untenable assumptions regarding the

¹ According to Richard (*Ann chim phys*, [8] 21, 391 (1920)) trimethyl-tert.-butyl glycol isomerizes by the migration of the smaller methyl radical to hexamethyl acetone. A comparison of the absolutely symmetrical structure of that product with that of the other possible ketone, i. e., $CH_3-CO-C(CH_3)_3C(CH_3)_3$, shows that it should have a much larger heat of formation, and this entropy factor probably out-balances that due to the larger energy factor involved in the migration of the methyl group. Theoretically, the formation of a mixture of the two *pinacolones* seems probable.

² Michael, *THIS JOURNAL*, 41, 197 (1919).

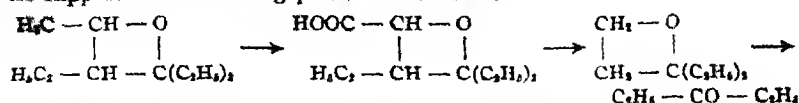
³ *Ibid*, 400-403.

⁴ *Monatsh.*, 28, 740 (1907).

⁵ *Ibid*, 764.

⁶ *Ibid*, 764.

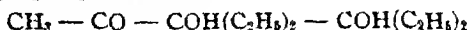
relation of the course of oxidation to chemical structure; for instance, he supposed the following phases of oxidation:



An oxide of the above structure must, in alkaline solution, in the primary phase, assimilate water to pass over into the β -glycol



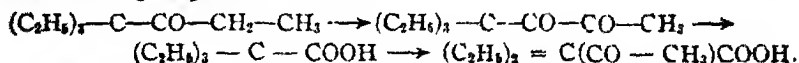
which, according to the above assumption, would be primarily oxidized by the conversion of the methyl into the carboxyl group.¹ But, the first stage must evidently consist in the oxidation of the secondary carbinol to the carbonyl group, *i. e.*, into



and then into



which salt should be stable towards the reagent under the conditions of the experiment. Samec's scheme of oxidation involves a series of impossible assumptions, and may be disregarded, as, even if it were accepted, it is incompatible with the formation of diethyl-acetoacetic acid. According to our present knowledge of the relation of oxidation by permanganate to chemical structure, the pinacolone should pass through the following stages of oxidation:²



The diethyl-acetoacetate thus formed hydrolyzes readily to diethyl-acetone and diethyl acetate, and the α -hydroxy-diethyl acetate is formed by oxidation of that salt, as R. Meyer⁴ has shown that the methinyl hydrogen in the salts of such tertiary acids is readily changed by permanganate into the hydroxyl group. There is, therefore, no cogent reason for accepting an oxide-structure for the product of rearrangement of any tetra-alkyl glycol, and only the pinacolone transformation is known.

Rearrangements in Aromatic α,β -Glycols.

A similar interpretation of the pinacol rearrangement in those α,β -glycols, where all the hydrocarbyl radicals are aromatic, would involve an *o*-hydrogen atom, which was theoretically improbable, as was shown

¹ According to this assumption, if a mixture of a fatty hydrocarbon, and a sec. carbinol derived from it, are oxidized, the hydrocarbon would be attacked before the alcohol, which obviously would not be the case.

² Glueckmann, *Monatsh.*, 10, 770 (1890); Wagner, *Ann.*, 298, 284 (1897). For explanation see Michael, *J. prakt. Chem.*, [2] 60, 355-362 (1899).

⁴ Michael *loc. cit.*

experimentally by Montagne.¹ The course of the structural changes proceeding in such aromatic glycols with the abstraction of water is complicated, being dependent on the character and the number of the aryl groups, but an insight into the mechanism of the rearrangements may be obtained by analysis from the affinity-energy standpoint.

When hydro- or isohydro-benzoin is boiled with a 40% solution of sulfuric acid a dehydration takes place with the formation of stereomeric tetraphenyl-diethylene oxides and of diphenyl-acetaldehyde.² The oxides (the so-called α -pinacolones) are dimeric,³ and are converted, by heating higher (200°) with the above solution, or with conc. hydrochloric acid (170°), into the aldehyde; but this transformation depends on the strength of the acid, since acetic acid (170°) gives the diacetate with the oxide, and a complicated decomposition results with the iso-oxide. Benzopinacol yields *benzopinacolone* on warming with benzoyl⁴ or acetyl⁵ chloride, and that the transformation is due to the catalytic and dehydrating capacity of the reagents is evident from the behavior of the pinacol towards 40% sulfuric acid, or acetic anhydride, at 200°, when decomposition by heat energy into benzophenone and diphenyl carbinol alone takes place.⁶ Quite a different behavior is shown by diphenyl-ditolyl pinacol; heated (160°) with 40% sulfuric, or conc. acetic acid, it yields a mixture of *pinacolone* and oxide, which, judging from analogy to the oxide from benzopinacol, is a monomeric product,⁷ and the oxide separates almost quantitatively at room temperature from an alcoholic solution, which is slightly acidulated by hydrochloric acid. A factor, decidedly conducive to the dehydration through the two hydroxyl groups of these glycols (Type B), is the property of aryl radicals to favor the substitution reactivity of the hydroxyl group in aryl substituted methyl alcohols.⁸ *i. e.*, to lessen the expenditure of energy required to separate it from the *hydrocarbyl* radical. They not only exert this influence to a far greater degree than any alkyl radical, but it increases in extent with the relative positive influence of the aryl group on the carbinol carbon atom.⁹ Further, the aryl more than the alkyl radical is susceptible to a shifting in the molecule, since it decreases the affinity of carbon to carbon to a greater degree, and this influence, too, is augmented with increasing positivity.³ These

¹ *Rec. trav. chim.*, 21, 30 (1902)

² Breuer and Zincke, *Ber.*, 11, 72 (1878)

³ Auwers, *ibid.*, 24, 1780 (1891)

⁴ Linnemann, *Ann.*, 133, 28 (1865)

⁵ Thoerner and Zincke, *Ber.*, 10, 1473 (1877)

⁶ Thoerner and Zincke, *loc. cit.*

⁷ Klinger and Lannes, *Ber.*, 29, 2158 (1896)

⁸ See Meerwein, *Ann.*, 396, 218 (1913); Tiffeneau, *Ann. chim. phys.*, [8] 10, 325 (1907).

relations manifest themselves, for instance, in the quantitative breaking down of benzopinacol at its melting point (204°) into benzophenone and diphenylcarbinol;¹ in the migration of the aromatic, and not the aliphatic, radical in the transformations of mixed pinacols,² and that the more positive of the aryl groups³ shifts its position in the molecule in a pinacol rearrangement.⁴ The intramolecular elimination of water in the sym.-diaryl-glycols tends, therefore, to proceed through the two hydroxyl groups,⁵ while the loss of water in the sym. dialkyl derivatives occurs through the utilization of a nuclear hydrogen atom and a hydroxyl group; and the hindrance to the migration of the *hydrocarbyl* radical is less in the aromatic derivatives. These two factors unite to cause the characteristic difference in the behavior of the sym. diaryl- and dialkyl- α,β -glycols; the aromatic substances yielding diaryl-acetaldehydes, by aryl migration, and oxides; while the latter class of compounds gives ketones. It is evident now why the structural change takes place more readily with ditolyl-diphenyl than with tetraphenyl-glycol, and why the more positive tolyl radical in the mixed glycol is the migrating group.⁴ In configurations the aryl-pinacol rearrangement may be represented by

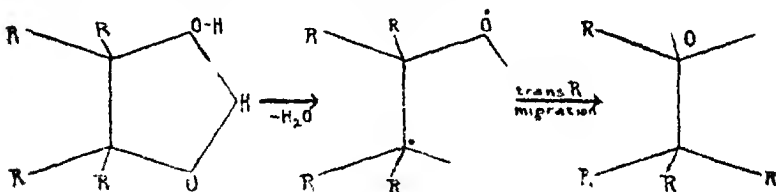


Fig. 6.

Characteristic of the aromatic glycols is the simultaneous formation of mono- or dimeric oxides. A clue to explain the different behavior of the aromatic and of the fatty glycols in this respect may be found in the stabilities of the oxides in the two series towards water. Ethylene oxide passes over into glycol when warmed with water, and the ease of conversion increases with the sym. replacement of the nuclear hydrogen by alkyl; enormously with unsym. substitution.⁶ On the other hand, the replacement by aryl groups gives oxides showing a stability increasing with the number of introduced radicals; indeed, the tendency to form a monomeric oxide increases with accumulation of aryl groups, as is seen, *e. g.*, by the

¹ Thoenner and Zincke, *Ber.*, 10, 1474 (1877).

² Tiffeneau, *Ann. chim. phys.*, [8] 10, 345 (1907); Parry, *J. Chem. Soc.*, 107, 108 (1915).

³ Michael, *loc. cit.*

⁴ Acree, *Am. Chem. J.*, 33, 180 (1905).

⁵ Meerwein, *loc. cit.*

⁶ Eltekow, *Ber.*, 16, 395 (1883); Michael, *J. prakt. Chem.*, [2] 60, 424 (1899).

formation of such a product from tetraphenyl-glycol,¹ and dimeric oxides from the stereomeric diphenyl derivatives.²

In respect to the role played by the reagents in the transformations of the aromatic glycols, the behavior of the substances quoted above show that it is of a catalytic nature. Although it is only secondarily due to the hygroscopic properties of the reagents, the energy required to separate water from the two hydroxyl groups (Type B) is much greater than in the other possible two directions ((A) and (C)), as is evident from the character of the reagents necessary to effect it. From this point of view, the capability of strong acids, or of extremely energetic reagents, like the acyl chlorides, to cause the chemical changes through the considerable free energy incorporated into the reacting system by the formation of "polymolecules," will be understood, and, also, that weak acids are without action, since, although they may be decidedly hygroscopic, they are not capable of uniting in this manner with the carbinols. We may also follow the conversion of the aromatic oxides into aldehydes or ketones by treatment with the chemically strong reagents; in these cases, too, it is the added energy in the "polymolecule" of oxide and reagent that enables the chemical metamorphosis.

Rearrangements in Aryl Iodohydrals.

Apparently in a close relationship to the hydrobenzoin rearrangement, are those occurring in aromatic compounds of the type $\text{Ar} \cdot \text{CHOH} \cdot \text{CH}_2\text{I}$, and derivatives formed by replacing one of the hydrogens in the methylene or that in the methinyl group, and both of these hydrogens, by *hydrocarbyl* radicals.³ On treating such a derivative with mercuric oxide, or with alcoholic silver nitrate, an elimination of hydriodic acid, with a migration of the aryl group to the carbon atom which held the halogen atom takes place, and the intermediate enol structure thus formed converts itself into the corresponding aldehyde, respectively, ketone. Tiffeneau,⁴ who discovered this interesting type rearrangement, discussed the possible explanations, and concluded that it takes place through the separation of the iodine and a hydrogen atom from the same carbon atom. *i. e.*, a unilateral elimination, and that the free valences in the unstable chemical system of the type $\text{Ar} \cdot \text{CHOH} \cdot \dot{\text{C}}\text{H}$ thus formed cause a shifting of the aryl group to the Δ -carbon atom. And, he supported the explanation by showing that compounds of the type $\text{Ar} \cdot \text{C}(\text{OE})\text{Alk} \cdot \text{CHI}(\text{Alk})$ are converted by mercuric oxide⁵ into $\text{Alk} \cdot$

¹ Klinger and Lonnes, *Ber.*, 29, 2158 (1896).

² Auwers, *Ibid.*, 24, 1780 (1891).

³ Tiffeneau. For the literature and a general discussion of the subject, see *Bull. soc. chim.*, [4] 2, 1205 (1907).

⁴ *Ibid.*, 1207-1212.

⁵ *Ibid.*, 1210.

$C(OE) = C(Ar)Alk$. There is a feature, however, in this class of type rearrangement which has not as yet been explained, *viz.*, that it depends on the chemical character of the reagent. It may be brought about by silver nitrate or by mercuric oxide, even with those iodohydrols whose chemical structures permit an ethylenic separation, *i. e.*, a bilateral elimination of hydriodic acid. But, with such substances, the reagent commonly used for this purpose, *i. e.*, alcoholic potash, abstracts the acid bilaterally to form ethylenic derivatives, without the occurrence of migrations; and, with the substitution of the halogen by ethoxyl, when ethylenic unsaturation is structurally precluded. This type of rearrangement depends, therefore, on specific properties in silver nitrate and in mercuric oxide, and a complete explanation must show why it is that only these reagents cause unilateral unsaturation. Mercuric oxide has the unique capacity of readily replacing hydrogen, that is directly joined to carbon, by mercury; less in evidence is this property with alcoholic silver nitrate, but the monoalkyl acetylenes yield the corresponding silver derivatives with the reagent.¹ It would seem, therefore, that the first phase in the Tiffeneau rearrangement consists in the conversion of $-C(OH)-CHI-$ into $-C(OH)-CAgI-$ or $(C(OH)-CI)_2Hg$, and that the formation of the unstable radical, $-C(OH)-\dot{C}-$, is due to the affinity between the metal and the halogen. It may be doubted, however, if the second phase would proceed in this manner, if a comparatively slight resistance to migration, as shown by the aryl group of $Ar-COH-$, did not exist in the molecule,² which assists in enabling the transformation to proceed with an increase of entropy.

Benzil Rearrangement.

Although this isomerization is one of the oldest known in organic chemistry,³ no satisfactory explanation of the change has as yet been given. According to Nef,⁴ benzil adds water to form a monohydrate, which breaks down into benzophenone and dioxymethylene, $C(OH)_2$; the latter product is supposed to assimilate water and give formic acid, which then adds to the carbonyl group of the ketone. A more hypothetical and impossible cycle of chemical changes is scarcely conceivable. In the first place, there is no indication of the formation of a hydrated benzil, but, even accepting its existence during the reaction, it is certain that alkali would rupture the carbon linkage between the carbonyl and the hydrated⁵ group, and in forming sodium benzoate and benzoic aldehyde, a further

¹ Behal, *Ann. chim. phys.*, [6] 15, 408 (1888); Bruylant, *Ber.*, 8, 410 (1875).

² For this reason the Tiffeneau rearrangement may not take place with the corresponding aliphatic iodohydrols

³ Liebig, *Ann.*, 25, 27 (1838).

⁴ *Ibid.*, 298, 372 (1897).

⁵ See page 814.

reaction could follow only on the latter product. Further, nothing would be gained by accepting the breaking up into benzophenone and dioxy-methylene, as the latter complex would either decompose into water and carbon monoxide, which could not possibly react on the ketone, or isomerize to formic acid, which would immediately be converted into formate, and by no stretch of the imagination may that salt be supposed to unite with the carbonyl group of benzophenone under the conditions of the rearrangement. Tiffeneau¹ assumes the addition of a molecule of alkali to each of the carbonyl groups, then an elimination of water from the addition product, and isomerization of the dipotassium oxo-ethylene derivative thus formed to dipotassium benzilate. Against this explanation it may be urged that there is no experimental evidence, nor is it probable, that benzil is capable of adding two molecules of alkali, or that benzoic acid forms a dibasic salt. Further, that our knowledge of the properties of the alkylene oxides indicates that Tiffeneau's hypothetical oxide, instead of being formed, would add water under the conditions of the rearrangement; and, even accepting its formation, the reason for and the mechanism of the process are no clearer than before.

Schroeter² supposes the primary formation of $C_6H_5-C(OK)OH-CO-C_6H_5$, which breaks up into $C_6H_5-C-CO-C_6H_5$ and $KO-OH$, then a rearrangement of the first complex into diphenylketene, which reacts on the metallic hyperoxide to form potassium benzilate. This construction is supposed to find an experimental support in the decomposition of azibenzil into nitrogen and diphenylketene.³

The analogy between the breaking down of the assumed benzil-alkali addition product and the azi derivative is only superficial. The azi group is distinguished by the readiness with which it separates from carbon, whereby the very considerable amount of free energy in the nitrogen group is, in passing over into free nitrogen, practically converted into bound energy and heat.¹ On the other hand, the substance $C_6H_5-C(OK)OH-CO-C_6H_5$, whose formation is due to the strive of the free negative energy in the carbonyl group and the positive of the alkali towards neutralization, and proceeds with the considerable conversion of the free energy of the system into bound energy and heat, would, in breaking up into $C_6H_5-C-CO-C_6H_5$ and $KO-OH$, form a system far richer in free energy; i. e., there would be a spontaneous degradation of entropy, which is not possible. Indeed, the extremely strong capacity of the divalent carbon atom to unite with oxygen, and the strong oxidizing power of potassium hyperoxide, makes the reverse reaction much more probable; that is, such a benzil addition product, instead of splitting

¹ *Rev. gén. Sci.*, 1907, 585.

² *Ber.*, 42, 2345 (1911)

³ Michael, *THIS JOURNAL*, 32, 991 (1910); *J. prakt. Chem.*, [2] 68, 487 (1903).

up, would be formed from Schroeter's hypothetical substance and potassium hyperoxide. Finally, diphenylketene has not been converted into benzoic acid, but with alcohol, which is present in the usual preparation of the benzilate from benzil, it passes over very readily into diphenylacetic ester, which compound, or the corresponding alkali salt, is not formed in the rearrangement.

The affinity of the carbon atoms of the carbonyl groups in benzil for each other has been greatly reduced by the attached oxygen atoms,¹ and the compound is easily ruptured in many of its reactions at that point. For instance, hydrocyanic acid possesses the catalytic property of causing certain organic substances to decompose at moderate temperatures, with the assimilation of water or alcohol. Benzil in alcoholic solution with nascent hydrocyanic acid at room temperature, or at a somewhat higher temperature with the aqueous acid, is split between the carbonyl groups and gives benzoic aldehyde and ester.² And, when it is treated with a strong soda solution and potassium cyanide, which mixture shares the catalytic properties of the acid, it is decomposed at ordinary temperature into benzoate and benzoic aldehyde.³ That benzil shows such a contrast in its stability towards water and prussic acid, or soda and the cyanide, and on heating with alcoholic, or very concentrated aqueous, caustic potash, is due to the conversion of the $\text{CO} - \text{CO}$ group under the latter conditions into $-\text{C}(\text{OK})\text{OH} - \text{CO}-$.⁴ Since the alkali practically neutralizes the negative energy in the carbonyl groups, it greatly increases the amount of energy required to separate the carbon atoms in these groups, while it decreases to a corresponding extent that necessary to rupture the carbon atom of the $\text{C}(\text{OK})\text{OH}$ from the phenyl group.⁵ This change in the affinity relations permits the reaction to proceed in a different direction, and with a far greater entropy increase, as, *instead of forming a mixture of the neutral benzoic aldehyde and a salt of the weak benzoic acid* ($K, 6.10^{-6}$), the system may now completely convert itself, by the trans-migration of phenyl and hydrogen, into a salt of the relatively strong benzoic acid ($K, 92.10^{-5}$),⁶ and the extent of the

¹ Michael, *THIS JOURNAL*, 32, 996 (1910).

² Michael and Palmer, *Am. Chem. J.*, 7, 190 (1885).

³ Jourdan, *Ber.*, 16, 659 (1883).

⁴ The violet coloration on treating benzil with alcoholic potash is undoubtedly due to the formation of an addition product, on heating the solution it disappears with the formation of benzilate and benzoate.

⁵ Michael, *THIS JOURNAL*, 32, 996-998 (1910). The influence of strong, positive chemical energy in decreasing the affinity of carbon for carbon is a subject that deserves far more attention in chemical theory than it has received, and a systematic experimental investigation of the subject would certainly yield results of great theoretical interest.

⁶ The spatial proximity (1,5) of the carbinol hydroxyl-oxygen and the acidic hydrogen in benzoic acid explains its large affinity constant (Michael, *THIS JOURNAL*, 34, 849 (1912); 40, 705 (1918).

neutralization of the great positive energy still remaining in the alkali is the dominating factor in the conversion of the free energy of the system into bound energy and heat. The isomerization of the benzil-alkali product may be represented by

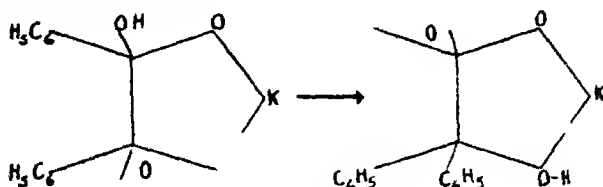


Fig. 7

This interpretation explains why benzilate is formed almost quantitatively, when benzil is fluxed with a large excess of alkali and but little water,¹ while with alcoholic potash more or less benzoate is formed at the same time. The alkali-benzil addition product cannot be very stable towards water, but must be hydrolyzed into benzil and alkali in a direct proportion to the amount of water present, and increase in its stability proportionately to the concentration of alkali. Towards alcohol such an easily hydrolyzed salt must be more stable than towards water, and the amount of alkali-addition compound must stand in a direct ratio to the concentration of the alcoholate and of the alcohol. In the decomposition of benzil under these varying conditions, the proportion formed of benzilate to benzoate must depend, therefore, on that of addition-product to benzil in the reacting mixtures.

Intermediate Products in Rearrangements.

The question of the possible existence of such substances in type rearrangements, as are assumed in some of the above reaction schemes, has been the subject of considerable discussion, and will be briefly considered at this place from the energy-spatial standpoint.²

¹ E. Fischer, *Ber.*, 14, 326, footnote (1881).

² The spatial factor in intramolecular rearrangements has not hitherto been taken into account; not even in other kinds of intramolecular reactions has it received nearly the consideration it merits. Its great importance is evident, when one considers that the bound energy acting through space between two atoms, stands, *cel. par.*, in an inverse ratio to this distance (THIS JOURNAL, 32, 999 (1910)).

A number of mechanical explanations of the rearrangement phenomenon have been given which are in direct opposition to the energy-spatial atomic relations, and which, for this reason, cannot be considered tenable. For instance, Lapworth (*J. Chem. Soc.*, 73, 448 (1898)) explains the change of $X-C_a-C_\beta=C_\gamma-Y$ into $Y-C_a-C_\beta=C_\gamma-X$, by supposing C_a to bend towards C_β , so that the single union between them passes over into double linkage, and by so doing X approaches C_γ so closely that it may pass over to it, along with the change of the double linkage between C_β and C_γ into single. A repetition of this process between C_γ and C_a is supposed to explain

The unstable structure in (A)¹ in the rearrangement of glycol may pass over, by the gyration of the methylene group, into vinyl carbinol (1), which in itself would not require a considerable expenditure of its free energy, but, along with the isomerization, a further conversion of free energy into bound energy and heat occurs at all the atoms although mainly at the carbon atoms with the formation of the so-called double linkage.² The conversion of the unstable structure into aldehyde (2) may proceed through that of vinyl carbinol (1), but that isomerization evidently depends upon the affinity of the methylene carbon for the migrating hydrogen. This relation may be so reduced by substituting the methylene hydrogens by strongly positive, or by negative radicals,³ that intermediate products of the vinol type become stable under ordinary conditions. The aryl group exerts such a positive influence, which explains the existence of $(C_6H_5)_2-C=C(OH)C_6H_5$ in a free state,⁴ and, also, that this substance, and not the isomeric keto derivative, is obtained in the elimination of water from triphenylglycol.⁵

The intermediate structure in type (B)⁶ evidently parts with much of its free energy in its transformation into aldehyde, ethylene or diethylene oxide; and, also, that in (C)⁶ in becoming a ketone; in the latter case, not only in the expenditure of energy involved in the migration of R and H, but because the free energy at the Δ -carbons is largely converted into bound energy and heat. It is evident that all these intermediate structures loose considerable of their free energy in passing over into the more stable forms, and, with this dynamic loss, the quality of the remaining rearrangements of this type, since X and Y have exchanged places in the molecule.

The explanation is founded on the disproven van't Hoff conception of double linkage (see *THIS JOURNAL*, 40, 705, 1674 (1918)), moreover, a considerable expenditure of energy would be required to bring the saturated groups centered about C_6 and then about C_7 into double union which occurs without any apparent connection to the free energy in the system. Further, the fruitless chase of X for Y, involving the overcoming of great energetic hindrances, is unnecessary, as these atoms or group of atoms are not, as represented in the Lapworth diagram, separated as far as possible in the molecule, but are in the spatially closest positions (1,5), without being in direct union. And, after all these improbable assumptions, we are no nearer to an explanation than before, as no reason has been given why they should occur. This criticism of the Lapworth hypothesis may be extended to many other attempts at explanations of organic changes that are based on the current mechanical conception of the valence phenomenon (see *THIS JOURNAL*, 32, 1007 (1910)).

¹ See page 794.

² Michael, *THIS JOURNAL*, 40, 705 (1918).

³ Michael, *ibid.*, 32, 995-998 (1910); *Ann.*, 363, 23 (1918).

⁴ Biltz, *Ann.*, 296, 242 (1898); *Ber.*, 32, 650 (1899); see Michael, *Ann.*, 363, 23 (1907).

⁵ Tiffeneau, *Compt. rend.*, 146, 29 (1908).

⁶ See page 796.

free energy, *i. e.*, the affinity values of the atoms or groups that may determine a further change, usually fall off in the same direction. For instance, it is obvious, that the unstable structure in (B) possesses, in the amount and nature of the free energy in its Δ -oxygen and its Δ -carbon, a greater capacity to isomerize into an aldehyde or a ketone, than the corresponding ethylene oxide does, and that a further decrease, but to a less degree, must be shown by diethylene oxide. It is this quantity and quality of the free energy in the intermediate form in (B) that enables the direct rearrangement, which, to bring about with the oxides, can be done only with the aid of extraneous chemical energy in a more or less considerable amount.¹

The experimental conditions in the rearrangements of the α,β -glycols are not favorable to the isolation of intermediate structures, but this is by no means impossible in some other classes of rearrangements.

Phenyl isonitrile isomerizes to the nitrile at a moderately high temperature,² and, if it were formed in reactions only proceeding at a higher temperature, the isonitrile would not be known. The actual temperature, however, to which a chemical structure is exposed at the moment of its formation is not the outward, measured by a thermometer, but the inward—"the internal maximum heat"³—existing before the heat energy generated by the interacting molecules becomes dissipated through the mass, and which must be considerably higher. Evidently, what are considered unstable chemical structures in some cases are so only in a relative sense, since chemical affinity is dependent on heat energy, and there can be no doubt that some of the intermediate, under the ordinary conditions of experimentation, unstable forms may be isolated, if the "internal maximum heat" may be controlled, and the reaction would take place under such conditions. For instance, silver enol-aceto-bromo-amide, answering to its affinity relations and its stereo structure, is a very unstable product,⁴ and it is by no means impossible that, with the highly favorable energetic-spatial relations existing in the halogen and metal for interaction,⁵ the decomposition may be conducted at a sufficiently low temperature to give stability to the assumed intermediate product, $\text{CH}_3 - \text{C}(\text{O})\text{N}$.

Unilateral Elimination and Rearrangement.

In several of the reactions considered above a one-sided elimination of a group of atoms, *i. e.*, separation from a single carbon atom, is assumed. As the theoretical bearing of this important subject has been obscured by

¹ See page 795.

² Weith, *Ber.*, 6, 213 (1873).

³ Wohl, *Ber.*, 40, 2290 (1907); Michael, *THIS JOURNAL*, 32, 992 (1910).

⁴ Mauguin, *Ann. chim. phys.*, [8] 22, 313 (1911).

⁵ See page 791.

untenable speculations,¹ it, too, will be considered briefly from the standpoint of the affinity-energy relations.

When hydrobromic acid is removed from ethyl bromide by means of an alkali, a bilateral elimination of its components takes place for the following reasons: the affinity of the relatively negative hydroxyl group of the alkali is greater for the hydrogen of the methyl group, because they are relatively positive to those in the CH_2Br radical, but the main factor is that ethylene must have much less free energy, *i. e.*, a larger heat of formation, than the isomeric ethylidene would have. This important energetic relation follows from the sphere-segment theory,² since in the formation of ethylene a further segmentation of the carbon atoms occurs, whereby a considerable amount of their free energy is converted into bound energy and heat,³ whereas in that to ethylidene, a further carbon segmentation is structurally excluded. These energetic relations are expressed in the following sphere-segment structures⁴



Fig. 8.

What are the structural and energy relations in an organic molecule that favor the existence of unilaterally unsaturated substances, and the unilateral elimination of a component part? It is obvious that such an unsaturated compound, with an enormous inherent motive power, than is actuated by a large content in free energy centered at a single carbon atom, should show at that point a great capacity for intermolecular carbon polymerization or for inducing an intramolecular rearrangement; in either case with a large increase in the entropy of the system. Any chemical change in the structure of a complex containing a unilaterally

¹ Nef, *Ann.*, 298, 202 (1897), 309, 126 (1899); 318, 1, 137 (1901); *THIS JOURNAL*, 26, 1549 (1904); 30, 645 (1908). Nef at first assumed ethylenic dissociation only, but this view led to conclusions that were irreconcilable with the most common chemical facts; *e. g.*, the same product of reaction should be formed with isomeric primary, secondary and tertiary halides (Michael, *Am. Chem. J.*, 25, 427-30 (1901)). There is no connection between the chemical nature and the structures of the substances and the course of the reactions in Nef's views, and his explanations mostly halt after the results of experimentation; that is, in stating to accord with them, that the process proceeds through ethylenic or methylenic dissociation, or in both directions (see Michael, *J. prakt. Chem.*, [2] 60, 471-479 (1899)). Moreover, many assumptions involved in his explanations are obviously impossible.

² *THIS JOURNAL*, 40, 705, 1674 (1918).

³ *Ibid.*, 40, 705 (1918).

⁴ The relative proportion of the bound energy between the carbon atoms is represented by the extent of the segmentations and the spheres represent the "co-volumes" or "vibratory volumes" of the atoms.

Δ -carbon atom, that diminishes the affinity of that Δ -carbon for itself, will decrease its tendency to react by intermolecular carbon polymerization. Such an influence is exerted by positive, and by negative, radicals; especially when they are in direct union with the Δ -carbon, and to an extent proportionate to the magnitude of the influence.¹ On the other hand, any change that diminishes the affinity of the unilaterally Δ -carbon for those atoms, or groups of atoms, in the molecule, that by migrating to it would form a more stable isomer, will decrease the tendency towards an intramolecular rearrangement to a corresponding degree. And the combined influence of both these factors may enable the unilaterally Δ -structure to exist in a free state.² The amount of free energy at the Δ -carbon atom of ethylidene, and its affinity for itself and for hydrogen, are evidently too developed for the stability of such a structure, and it must either spontaneously polymerize to 2,3-butylene or isomerize to ethylene. It is a well-known fact that aryl radicals exert an extremely strong positive influence on any atom joined directly to them and that they, therefore, reduce the affinity of such atoms for each other very materially. The separate existence of fully substituted, aryl derivations of methyl, and of similarly constituted nitrogen products, are, therefore, interesting confirmations of the theory.³ And, since negative radicals also tend to inhibit carbon polymerization,⁴ there is no theoretical reason why a system like $C(NO_2)_2$, or perhaps one in which nitroxyl is replaced by a less strong negative radical, should not have a free existence.

As a further illustration, the formation of phenylisonitrile from aniline and chloroform will be analyzed, where the motive power is the affinity of the alkali for the halhydric acid, and which proceeds through the following phases:



The large free energy content in the isonitrile⁵ manifests itself in its chemical properties, and the unilaterally, unsaturated compound is stable under ordinary conditions for the following reasons: A carbon polymeriza-

¹ THIS JOURNAL, 32, 996 (1910).

² *J. prakt. Chem.*, [2] 60, 298, 478 (1899).

³ THIS JOURNAL, 32, 997 (1910).

⁴ *Ibid.*, 996

⁵ It is interesting to note that Gautier (*Ann. chim. phys.*, [4] 17, 209 (1869)), who discovered the aliphatic carbylamines, assigned them the divalent carbon structure.

⁶ This reaction proceeds exothermally with a large increase in the entropy of the system; the increase of free energy in the isonitrile is slight in comparison to the decrease accompanying the neutralization of the hydrochloric acid by the base. The formation of the isonitrile, energetically the *extropic* (THIS JOURNAL, 40, 1707 (1918)) part of the reaction, is forced, as through it lies the only way that the system can realize the condition of maximum entropy. Similar energetic relations are frequent in organic reactions.

tion to $C_6H_5-N=C=C=N-C_6H_5$ appears possible from the valence viewpoint, but its formation is enjoined by the reduction of the affinity between the Δ -carbon atoms by the negative nitrogen radical; similarly, an oxygen atom prevents the carbon polymerization of carbon monoxide. Another valence possibility would be realized in a carbon-nitrogen polymerization, to yield a 4- or a 6-membered ring derivative containing divalent carbons. The spontaneous formation of tetracyclic ring compounds by polymerization is of rare occurrence; it takes place only when a very great difference exists in the polarity of the Δ -atoms, as is the case in $CH_2=C(COOEt)_2$, which is also an essential condition for a facile polymerization to a hexacyclic derivative.¹ Further, the production of either of these ring derivatives is not favored by the comparatively weak affinity relations between the unsaturated carbon and nitrogen atoms.

Generally speaking, there is theoretically no energetic obstacle to the chemical breaking up of an organic substance by unilateral elimination, and it is of rare occurrence only because, for reasons given above for the formation of ethylene from ethyl bromide, a greater entropy increase goes along with the bilateral procedure. Such a one-sided unsaturation may be brought about, however, by so changing the structure of a substance, that no two of the groups in direct union contain atoms or groups of atoms that show more than a very slight affinity for each other, or for the reagent used in the reaction; while conditions favorable for the separation of a component part exist in a group with a single carbon atom. And, the relative ease with which such a unilateral elimination takes place will depend on the affinity of the reagent for the removed part, and on the expenditure of energy essential for the elimination, which evidently, is a constitutive factor.

For instance, benzyl bromide reacts with alcoholic potash by substitution and yields benzyl ethyl ether, but, with the introduction of an *o*-, or a *p*-nitro group, the reaction proceeds partially with the formation of dinitro stilbenes.² Nitroxyl is the strongest known negative radical, and in these positions greatly reduces the affinity of the carbon in the CH_2Br group for the hydrogens and also for the halogen. This influence, in decreasing the energetic hindrance to the elimination of halhydric acid, evidently favors its separation from the molecule, but the negative influence on the carbon atom does not suffice to prevent the polymerization of two molecules of the intermediate products, $C_6H_4(NO_2)CH$, to the stilbene derivatives. It is theoretically not impossible, however, that a greater accumulation of negative influence, perhaps that of two nitro-

¹ Michael, *J. prakt. Chem.*, [2] 60, 437-443 (1899)

² Strakonch, *Ber.*, 6, 328 (1873), Bischoff, *ibid.*, 21, 2072 (1888); Filbe and Bauer, *J. prakt. Chem.*, [2] 34, 344 (1886)

groups in *ortho* positions, may inhibit carbon polymerization sufficiently to give stability to the intermediate methylene derivative. Or, the conversion of $C_6H_5-CHOH-C(CH_3)_2-COOEt$, into $C_6H_5-C(COOEt)=C(CH_3)_2$ by dehydration with phosphorus pentoxide.¹ Methyl alcohol is not eliminated in this reaction, owing to the very considerable expense of energy required to separate the methyl group from the carbon atom, while the unilateral elimination of water is facilitated by the phenyl and the carboxyl group in decreasing the affinity between the carbinol-carbon and the hydrogen and hydroxyl. The great reservoir of free energy at the Δ -carbon in the intermediate structure, $C_6H_5-\ddot{C}-C(CH_3)_2-COOEt$, induces a rearrangement, in which the carboxyl, and not one of the methyl groups, migrates, because the energy required to separate the first group from carbon is less, and, because the heat of formation of the substance thus formed is probably greater than that of the isomeric ester.

The subject of organic rearrangement is far too comprehensive for treatment in a single paper, but it is believed that the analysis of typical reactions given above will suffice to enable the application of the affinity-energy spatial viewpoint to other chemical transformations of this nature without difficulty.

CAMBRIDGE, MASS

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

THE ORIGIN OF THE HUMIN FORMED BY THE ACID HYDROLYSIS OF PROTEINS. V.²

By ROSS AIKEN GORTNER AND GEORGE E. HOLM.

Received January 12, 1920

Our earlier contributions to the subject of humin formation³ have led us to draw the conclusion that the formation of the black acid-insoluble humin on protein hydrolysis is due almost wholly to the interaction of tryptophane with some aldehyde or ketone and that no other known amino acid enters into the reaction to any appreciable extent. All of our earlier data have, however, involved the use of proteins, some of which were known to contain tryptophane, others from which this amino acid is supposed to be absent. By the addition of tryptophane to the latter, humin formation was markedly increased and we were unable to find any other group of compounds which would cause this increase excepting those con-

¹ Blaise and Courtot, *Bull. soc. chim.*, [3] 35, 589 (1906).

² Published with the approval of the Director as Paper No. 193, Journal Series of the Minnesota Agricultural Experiment Station.

³ *This Journal*, 37, 1630-1636 (1915); *J. Biol. Chem.*, 26, 177-204 (1916); *THIS JOURNAL*, 39, 2477-2501 (1917); *ibid.*, 42, 632 (1920).

taining an indole nucleus. Nevertheless the fact remained that there was still a possibility of error in our chain of evidence due to the fact that it was necessary for us to assume that the proteins with which we were working either contained or did not contain certain amino acids. It was likewise possible that they contained substances which inhibited humin formation.

While a large mass of data has been accumulated regarding the nature of the protein molecule, there are many things still to be elucidated; and it is, therefore, unsafe to assume too much regarding the amino acid content of a protein, like gelatin for example, when the known amino acids actually separated total only a 44.6% recovery.¹ Our inadequate knowledge of the protein molecule is still further demonstrated by the recent discovery of Dakin,² who found 10.5% of β -hydroxyglutamic acid in casein. This finding is all the more remarkable because of the fact that it was found in such quantities in casein, a protein which has been more exhaustively studied than any other.

We recognized this weakness in our argument and stated.¹ "We are, therefore, firmly convinced that of all the known hydrolytic products of proteins, tryptophane alone is concerned in the reaction which produces black insoluble humin, but that this reaction cannot take place without the presence of some as yet unidentified component of the protein molecule. There is, however, one further method of testing this statement, *i. e.*, to prepare all of the known amino acids in an absolutely pure form and then mix them in different combinations and boil these with hydrochloric acid both with and without the addition of aldehyde. If (a) pure tryptophane plus all of the other known amino acids does not produce a trace of insoluble humin when boiled with hydrochloric acid, but does produce humin when aldehyde is added and if (b) all the amino acids excepting tryptophane do not produce a trace of black insoluble humin either with or without the addition of aldehyde and if (c) tryptophane plus aldehyde produces the humin with the same ease when used alone or in the presence of any or all of the other pure amino acids, then our thesis will be definitely proven." We have now completed this experiment and this paper details the results.

Experimental.

As indicated above, our problem was to ascertain the amino acid responsible for humin formation when a protein is hydrolyzed by strong acids. Inasmuch as one can never be sure of the exact quantity of each amino acid which is present in a given protein, we have prepared 15 amino

¹ R. H. A. Plimmer, "The Chemical Constitution of the Proteins I. Analysis." Longmans, Green and Co., 1912, p. 61.

² *Biochem. J.*, 12, 390-317 (1918).

³ *THIS JOURNAL*, 39, 2498-9 (1917).

acids from various sources and by various methods and, after assuring ourselves of their purity, we have mixed them in certain combinations and subjected the mixtures to acid hydrolysis¹ both alone and in the presence of formaldehyde. We had hoped that we could make the experiment using all of the known amino acids, but at the time of making the experiments we did not have certain of the rarer ones, such as oxyproline, oxytryptophane, dioxydiamino-suberic acid, diaminotrioxo-dodecanoic acid and the new oxyglutamic acid. We did, however, have 15 amino acids at our disposal and inasmuch as the results which we obtained are so completely in accord with our earlier findings, we are convinced that the results would be unchanged even if the remaining amino acids had been included. Oxytryptophane would probably act like tryptophane, and the others would certainly react similarly to their analogues which we tested. The amino acids which we used, their source and the quantity which was present in each of the 4 hydrolyses, are given in Table I. In addition to the amino acids given in this table, tyrosine was added in Expts. I, II and III, and tryptophane was added in Expts. I and II. The plan of the experiment was as follows:

Expt. I.—To the 13 amino acids listed in Table I were added 0.1000 g. of tyrosine (7.74 mg. of amino nitrogen) and 0.1000 g. of tryptophane (6.86 mg. of amino nitrogen and 6.86 mg. of non-amino nitrogen). After adding 100 cc. of 20% hydrochloric acid the mixture was boiled for 24 hours, using a reflux condenser. This experiment corresponds to the hydrolysis of a protein of the composition shown in the second column of Table II. The hydrolysate was then analyzed more or less completely according to the Van Slyke method² with the modification that the humin fraction was estimated in 3 parts, as we have already suggested should be done.³

The data resulting from this analysis are shown in Table III.

Expt. II.—Expt. I (using all 15 amino acids) was repeated with the exception that 0.10 g. of formaldehyde (in the form of trioxymethylene) was added before the hydrolysis began. We have already pointed out⁴ the fact that formaldehyde in small quantity markedly increases the amount of humin nitrogen formed in a protein hydrolysis when certain amino acids are known to be present. The percentage composition of the mixture hydrolyzed is given in Table II. The analytical data are shown in Table III.

¹ Perhaps "hydrolysis" is a misnomer in this instance inasmuch as the amino acids are no longer combined with each other in peptide linkages.

² *J. Biol. Chem.*, 10, 15-55 (1911), 12, 275-284 (1912).

³ *This Journal*, 39, 2480 (1917).

⁴ *Ibid.*, 39, 2477-2501 (1917).

Expt. III.—To the 13 amino acids enumerated in Table I we added 0.1000 g. of tyrosine (7.74 mg. of amino nitrogen) and 0.10 g. of trioxymethylene. The mixture was then boiled with 100 cc. of 20% hydrochloric acid for 24 hours. It will be noted that Expt. III differs from Expt. II only in the fact that no tryptophane was present. The percentage composition of the mixture hydrolyzed here is given in Table II. The analytical data on this hydrolysate are shown in Table III.

Expt. IV.—To the 13 amino acids listed in Table I we added 0.10 g. of trioxymethylene and boiled with 20% hydrochloric acid for 24 hours. This experiment differs from Expt. II in that neither tyrosine nor tryptophane was present. The percentage composition of the mixture hydrolyzed is shown in Table II and the analytical data on the resulting solution are shown in Table III.

TABLE I.—SHOWING THE AMINO ACIDS USED IN THIS INVESTIGATION, THEIR SOURCES, THE QUANTITIES USED IN EACH EXPERIMENT, AND THE MILLIGRAMS OF AMINO NITROGEN AND NON-AMINO NITROGEN PRESENT

Amino acid.	Source	Amount used in each experiment G	Total, N. Mg	Amino, N. Mg	Non-amino, N. Mg
Aspartic acid.	Kahlbaum	0.1250	13.16	13	16
Arginine*	Gelatin and casein	0.0562	18.10	4.53	13.57
Alanine.	Silk	0.1250	19.66	19	66
Cystine.	Human hair	0.2500	29.13	29.13	. .
Glutamic acid hydrochloride	Gelatin and casein	0.2000	15.20	15	20
Glycine.	Silk	0.2500	46.65	46	65
Histidine dihydrochloride	Blood	0.2500	46.05	15.35	30.70
Leucine.	Gelatin and casein	0.1250	13.36	13	36
Lysine dihydrochloride.	Gelatin and casein	0.0300	3.84	3.84	. . .
Proline.	Gelatin and casein	0.0500	5.88	. . .	5.88
Phenylalanine hydrochloride. . . .	Gelatin and casein	0.1250	8.69	8.69	. . .
Serine.	Synthetic	0.1250	16.68	16	68
Valine.	"	0.1000	11.96	11	96
Unknown*			4.52	1.84	2.68
Total.		1.8112	252.88	200.05	52.83

* Our arginine was prepared by the Kossel separation. Inasmuch as we could not use the nitrate or picrolonate to separate it because of the nitrogen contained in these salts, we tried to prepare a pure hydrochloride but experienced difficulty in procuring sufficient crystalline material. We therefore used our arginine fraction in this work, analyzing the solution for arginine by Van Slyke's method, and found that while it was largely arginine it also contained a small amount of some other amino acid. This is certainly one of the bases for the arginine was precipitated twice by phosphotungstic acid before the silver separation was made. This residual nitrogen is reported in the table as "unknown."

^b We are indebted to Dr. C. O. Johns of the Bureau of Chemistry for this sample of valine.

TABLE II—SHOWING THE PERCENTAGE COMPOSITION OF THE MIXTURE OF AMINO ACIDS ANALYZED IN EXPTS I-IV INCLUSIVE.

	Percentage of each acid present in		
	Expts I and II	Expt III	Expt IV
Aspartic acid	6.65	7.03	7.45
Arginine	2.99	3.16	3.35
Alanine	0.65	7.03	7.45
Cystine	13.31	14.05	14.89
Glutamic acid	8.53	9.01	9.55
Glycine	13.31	14.05	14.89
Histidine	9.05	9.56	10.13
Leucine	6.65	7.03	7.45
Lysine	1.06	1.12	1.19
Proline	2.66	2.81	2.98
Phenylalanine	5.45	5.76	6.10
Serine	6.65	7.03	7.45
Valine	5.32	5.62	5.96
Unknown ^a	1.06	1.12	1.19
Tryptophane	5.32		
Tyrosine	5.32	5.62	
Total	90.96	100.00	100.03

^a Calculated as $\frac{1}{2}$ lysine and $\frac{1}{2}$ histidine.

TABLE III—SHOWING CERTAIN OF THE ANALYTICAL DATA OBTAINED IN EXPTS I TO IV

	Expt I	Expt II	Expt III	Expt IV
Ammonia N	1.80	0.80	3.90	4.50
Insol. humin N	0.00	13.10	0.00	0.00
Sol. humin N	0.20	5.00	5.40	0.20
Phosphotungstic acid humin N	5.30	3.98	3.20	3.15
N in bases	84.50	60.08	89.80	77.00
Amino N in bases	46.44	13.10	28.65	13.22
N in filtrate from bases	179.20	186.00	150.08	165.50
Amino N in filtrate from bases	173.46	177.42	145.80	160.87
Total N recovered	271.00	268.96	252.38	250.33
Per cent N recovered	98.78	98.04	96.84	99.00

Color Observations.—After the completion of the 24 hours' boiling there were marked differences in the appearances of the solutions in the flasks. No. II was an intense black color, being caused by solid black particles suspended throughout the solution. No. I contained no solid particles but had a dark red-brown color. No. III was light red-brown but contained no solid particles, while No. IV was a clear light straw-colored solution.

After the removal of the "soluble humin" by calcium hydroxide certain differences were still apparent. No. I was still a fairly dark red-brown solution, No. II was distinctly red-brown, but much lighter than No. I, No. III was a still lighter red-brown and No. IV was a very pale yellow.

Upon the addition of phosphotungstic acid all color was removed from each of the solutions,¹ the resulting filtrates being the pale straw color usually obtained. The basic phosphotungstates were white in Expts. III and IV, but distinctly grayish in Expts. I and II. This color was retained by the barium phosphotungstate precipitate which was buff colored in the case of Expts. I and II and practically white in the case of Expts. III and IV. The nitrogen remaining in this precipitate has been reported in our tables as "Phosphotungstic acid humin."²

Discussion.

The Acid Insoluble Humin.—It is this fraction with which we are principally concerned. It will be noted by reference to Table III that *the only experiment which yielded any insoluble humin nitrogen was that in which both tryptophane and aldehyde were present and that the nitrogen secured in that fraction amounted to 95.5% of the tryptophane nitrogen which had been added.* There can be no further doubt, therefore, but that the black insoluble humin of protein hydrolysis is derived from tryptophane. We are still in doubt as to the exact nature of the chemical reaction by which humin is produced in the hydrolysate of a purified protein. Whether or not this reaction is identical with that caused by the deliberate addition of an aldehyde to the hydrolysate can only be determined when we know the structure of the resulting products formed in the two cases, and we are continuing our investigations along that line.

The Acid Soluble Humin.—We have presented certain evidence in our earlier paper³ which indicated that the "soluble humin" was derived from tyrosine. It will be noted that in our present experiments *only those hydrolysates which contained both tyrosine and aldehyde yielded appreciable amounts of soluble humin.* The recovery was not quantitative due to the appreciable solubility of this soluble humin. Another method of demonstrating that the soluble humin is derived from tyrosine would be to determine the amount of tyrosine remaining in the "filtrate from the bases" in each experiment. Folin and Denis⁴ have proposed a method for the colorimetric estimation of tyrosine. We have utilized this method in estimating the tyrosine remaining in our "filtrates from the bases" and find the following figures for Expts. I, II and III after correcting the readings by subtracting the value of such color as was developed in the filtrate from the bases in Expt. IV where no tyrosine was added:

¹ The color was the first material to precipitate when phosphotungstic acid was added and this portion of the precipitate did not redissolve when the flask containing the precipitated bases and solution was warmed on the water bath.

² For a discussion of this fraction see Gortner and Holm, *THIS JOURNAL*, 39, 2485 (1917).

³ *Ibid.*, 39, 2485 (1917).

⁴ *J. Biol. Chem.*, 12, 245-251 (1912).

Expt	Tyrosine added Mg	Tyrosine found. Mg
I.	100	98.93
II	100	None
III	100	None

These figures, taken in conjunction with the figures for soluble humin nitrogen, prove conclusively that that fraction is produced by the interaction of tyrosine and the aldehyde.

The Phosphotungstic Acid Humin.—Our present series of experiments gives no clue as to the origin of this fraction inasmuch as it is present in all experiments in about equal amount. It may represent only an adsorption phenomena.

The Ammonia Fraction.—This fraction presents certain very interesting figures. It has been commonly supposed that cystine is quite readily deaminized by acid hydrolysis, but our data do not confirm this belief. The 1.80 mg of ammonia nitrogen in Expt. I represents pure deamination. The larger figures in Expts. III and IV represent the increase in volatile amines, etc., due to the presence of formaldehyde in the hydrolysate¹ while the *decrease* in ammonia in Expt. II is an exact duplication of our findings when a protein containing tryptophane (fibrin) was hydrolyzed in the presence of formaldehyde.² Further work must be done before this interesting phenomena is elucidated.

Summary.

In order to secure further evidence on the nature of humin formation, 15 pure amino acids were mixed in various proportions and boiled with 20% hydrochloric acid both in the presence and in the absence of formaldehyde. The following conclusions are evident:

1. The black insoluble humin is derived from tryptophane, and when the proper amount of aldehyde is present is a quantitative measure of the tryptophane present.
2. The "soluble humin" formed in the presence of formaldehyde is derived from tyrosine. It is not a quantitative measure of the tyrosine, due to the appreciable solubility of the resulting humin.
3. No evidence was secured as to the nature of the "phosphotungstic acid humin."
4. Cystine was not readily deaminized under the conditions of the experiments.
5. When both tryptophane and formaldehyde are present in the proportions necessary for the maximum formation of insoluble humin there is less deamination, as measured by ammonia formation, than when either the aldehyde or the tryptophane is absent from the hydrolysate.

ST. PAUL, MINNESOTA

¹ Gortner and Holm, *THIS JOURNAL*, 39, 2486 (1917).

² Gortner and Holm, *loc. cit.*, p. 2481, Fig. 1.

HAROLD C. CHEETHAM AND JOHN H. SCHMIDT.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

AN IMPROVED METHOD FOR THE PREPARATION OF PRIMARY ARSANILIC ACID.¹

BY HAROLD C. CHEETHAM AND JOHN H. SCHMIDT

Received January 13, 1920

Introduction.

Until recently the literature on arsanilic acid, though extensive, has been rather meager as regards the exact details for preparing the acid. Lately Fichter and Elkind² have given brief directions, and Kober³ has described in detail a method for which he claims a 30% yield. We have obtained, however, only fair results using Fichter and Elkind's method and decidedly poorer results following Kober's directions.

The usual procedure in making arsanilic acid is to heat arsenic acid in an excess of aniline at 180° or higher for 2 or 3 hours. After conducting numerous experiments we have found that it is distinctly advantageous to use a large excess of aniline, thus keeping the reaction mixture fluid, and to work at lower temperatures and increase the time of the reaction, thus avoiding the formation of tarry impurities. The final procedure adopted is as follows:

Experimental.

Preparation of Reagents.—The arsenic acid was prepared by either of the following methods.

1. Pure arsenious oxide was oxidized with nitric acid. The resulting solution was evaporated over a free flame until the temperature of the liquid was 160°. It was then evaporated to dryness by heating in an electric oven at 120°.

2. Pure arsenic pentoxide (As_2O_5) was dissolved in water and the solution concentrated over a free flame and dried as in 1.

Crude arsenic acid (76%) evaporated as in 1 may be used. The aniline was dried over caustic and redistilled.

Procedure.—47 g ($\frac{1}{2}$ mol.) of dry arsenic acid was placed in a 300-cc. Kjeldahl flask, 152 cc ($\frac{2}{3}$ mol) of aniline added and the mixture heated in a paraffin bath for 12 hours. The temperature of the bath was kept at 150°–160°. At a temperature of about 110° the mixture solidified and then slowly melted and remained liquid throughout the subsequent heating. After heating, the mixture was poured into an 800 cc. beaker and the flask rinsed out with 200 cc. of hot water, the rinsings being added to the beaker. 60 cc. of 6 *N* sodium hydroxide solution was then poured

¹ This work was done under the Grant of the U. S. Interdepartmental Social Hygiene Board, of Washington, D. C., Dr. T. A. Storey, Secretary.

² *Ber.*, 49, 239 (1916).

³ *This Journal*, 41, 451 (1919).

into the flask, removing by this means any last traces of the product, and then added with vigorous stirring to the reaction product which had been cooled to room temperature. The whole was now poured into a separatory funnel. The upper layer consists mainly of aniline, from which 90% of the excess aniline used can be recovered by steam distillation. The lower layer containing the sodium arsanilate was drawn off into a beaker 15-20 g. of infusorial earth was added and the solution filtered by suction, removing by this means any suspended aniline. To the filtrate, which was very light pink or colorless, 50 cc. of 6 *N* hydrochloric acid was added, and on standing a short time the arsanilic acid separated out as a colorless, finely crystalline precipitate. It was often necessary to stir the filtrate vigorously as there is a marked tendency for it to become supersaturated. Congo red paper may be used to indicate when sufficient acid has been added.

The filtered precipitate is pure enough for most purposes. However, it was usually recrystallized once from hot water with the addition of a small amount of animal charcoal. Prepared thus the product was usually perfectly colorless. The average yield of dry, recrystallized product was 26%.

The results of several analyses are given below, the samples having previously been dried under diminished pressure at 60°. The nitrogen was determined by the Kjeldahl-Gunning method, the arsenic by Ewins¹ method, the latter slightly modified in that the iodine used for titration was standardized each time against a blank to which a known amount of arsenious oxide had been added.

	As %	N. %		As %	N. %
Product Sample A . . .	33.61	6.30	Product Sample B . .	34.57	6.35
'	34.37	6.32		34.11	6.39
	33.76			34.58	6.35
	<hr/>			<hr/>	
Averages,	33.91	6.31	Averages,	34.42	6.36
Calc.. As, 34.60%; N, 6.45%.					

Conclusions.

The process described seems simpler than any heretofore published and can be carried out fairly economically, since 90% of the excess aniline can easily be recovered. The yields are as good as if not better (since they are based on pure dried recrystallized product) than those obtained by other investigators. We advise against making the arsanilic acid in large amounts unless efficient stirring is provided for.

MADISON, WIS.

¹ *J. Chem. Soc.*, 109, 1356 (1916).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

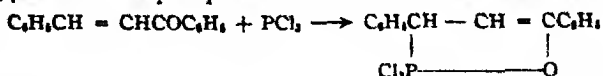
A NEW TYPE OF ADDITION REACTION.

BY JAMES B. CONANT AND ALAN A. COOK.

Received January 20, 1920

I. Introduction.

It was shown in a preliminary paper¹ that a keto-phosphonic acid was formed by the interaction of phosphorus trichloride, an α,β -unsaturated ketone and glacial acetic acid. By substituting acetic anhydride for the acid it has been possible to prove that the first step in the reaction consists of the 1,4-addition of phosphorus trichloride to the unsaturated ketone:

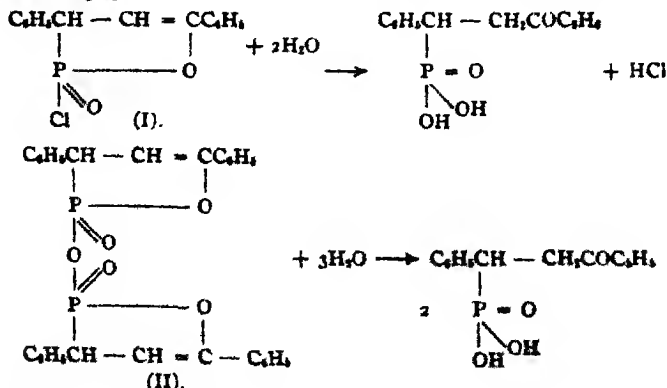


Such an addition is novel in that it involves adding only a single atom instead of the usual 2 atoms or groups. This single atom by increasing its valence unites with the ends of the conjugated system.

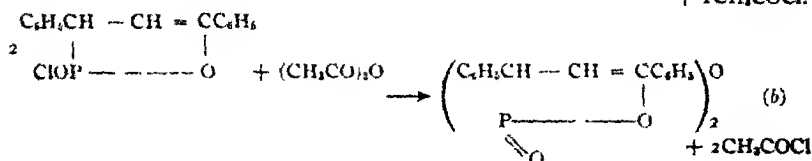
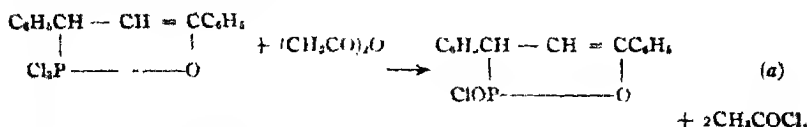
The mechanism of this reaction was difficult to establish because the reaction is reversible, the product is as sensitive as phosphorus pentachloride, and most reagents not only attack the chlorine atoms, but also open the ring. However, with acetic anhydride it was possible to obtain products in which the ring was still intact and to prove definitely their structure.

The Intermediate Products Formed with Acetic Anhydride.

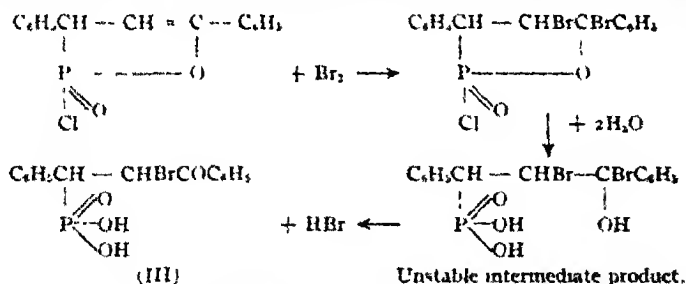
Phosphorus trichloride, benzal-acetophenone, and acetic anhydride react rapidly at room temperature giving acetyl chloride and a material which readily reacts with water, producing the keto-phosphonic acid. This intermediate product was obtained as a thick oil. It is a mixture of 2 substances—an acid chloride (I), and an acid anhydride (II). With water these compounds immediately form the keto-phosphonic acid described in the earlier paper:

¹ THIS JOURNAL, 39, 2679 (1917).

The hydrogen chloride produced in this reaction is a measure of the relative amounts of acid chloride and acid anhydride. If one molecule of acetic anhydride is employed in the initial reaction, the product is the acid chloride (I); if an excess is used various amounts of the anhydride (II) will also be formed (Equation b).

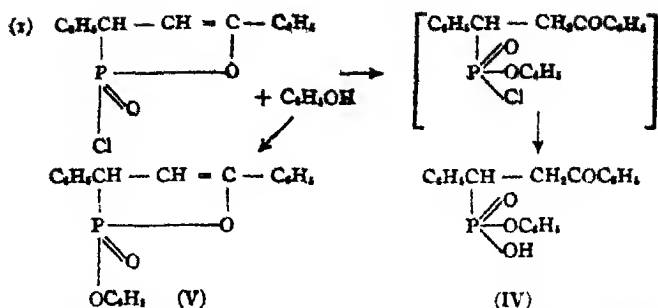


The acid chloride and the acid anhydride are both unsaturated compounds. This follows from the fact that they combine with one molecule of bromine without the evolution of hydrobromic acid. The position of the double linkage was established by treating the resulting dibromide with water, a β bromoketo-phosphonic acid (III) and hydrogen bromide were formed. The equation for the reaction of the acid chloride is as follows (with the anhydride the reaction is, of course, essentially the same):

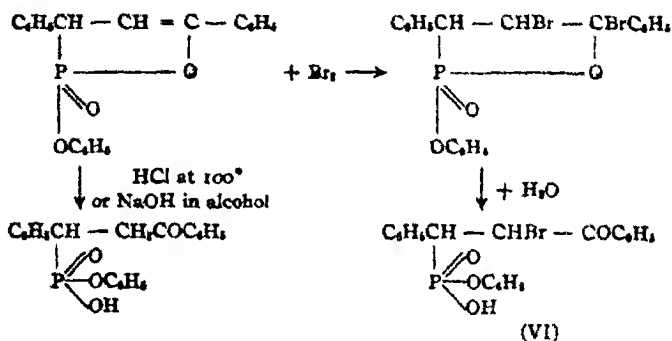


Phenol reacts with the acid chloride forming 2 substances—a mono-phenyl ester of the keto phosphonic acid (IV) and a phenyl ester of an unsaturated cyclic acid (V). In the first case the ring is opened (probably by the hydrogen chloride), but in the second the acid chloride is simply transformed into the corresponding phenyl ester.

The constitution of the ester represented by Formula V was established in exactly the same way as that of the acid chloride (II). The substance is an unsaturated cyclic compound because it combines with bromine and because it can be transformed by acids or bases into the monophenyl ester of the keto-phosphonic acid. The ring is more stable in this ester



than in the acid chloride. The position of the unsaturation was shown by transforming the bromine addition product into a monophenyl ester of the β -bromoketo-phosphonic acid (VI). These transformations are summarized below:



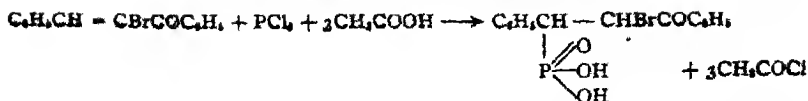
The nature of the intermediate product formed when acetic anhydride is used, is thus definitely established. The reactions with water, bromine and phenol conclusively prove that the material is a mixture of 2 unsaturated cyclic compounds—one an acid chloride, the other the corresponding anhydride. Both of these compounds contain the linkage



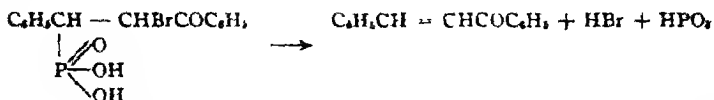
since they are still unsaturated although formed by an addition reaction and since they combine with water forming the keto-phosphonic acid.

Structure of the Bromine Compounds.

The structure of the β -bromoketo-phosphonic acid (III) and its monophenyl ester (VI) is of importance since the position of the double bond in the intermediate compounds was established by reference to these substances. The position of the bromine atom was shown by synthesizing these substances from α -bromobenzal-acetophenone, phosphorus trichloride and glacial acetic acid:



The β -bromo acid (which can also be prepared by bromination of the keto-phosphonic acid) is unstable in aqueous solution. It decomposes slowly into benzal-acetophenone, hydrogen bromide, and metaphosphoric acid



This decomposition is instantaneous in alkaline solution. It is similar to the loss of hydrobromic acid and carbon dioxide from such β -bromo acids as β -bromo hydrocinnamic acid. Fortunately the phenyl esters of the acid are much more stable and the monophenyl ester can be dissolved in sodium carbonate without decomposition. These esters are readily formed from the acid by the action of thionyl chloride and phenol.

Because of its sensitiveness, the β -bromo acid could not be isolated from the product of the reaction of phosphorus trichloride on the bromobenzal-acetophenone. The crude material was, however, treated with thionyl chloride and phenol and thus converted into the more stable monophenyl ester (VI) which could be obtained in a pure condition. This ester was identical with that obtained from the transformations of the cyclic ester (V), it was also identical with the ester prepared from the β -bromoketo-phosphonic acid. This acid, in turn, was shown to be the same whether prepared by bromination of the keto-phosphonic acid or from the dibromide of the cyclic acid chloride. The structure of all the bromine compounds involved in this work was thus established.

The Mechanism of the Reaction.

The structure of the compounds formed with acetic anhydride (I and II) proves conclusively that the fundamental process in the reaction is the addition of the phosphorus atom to the ends of the conjugated system. This addition involves the increase of valence of the phosphorus atom from 3 to 5. It is the type of addition reaction illustrated by the combination of phosphorus trichloride and chlorine or ammonia and hydrogen chloride. Such addition reactions, involving the increase of valence of one atom, are rare in organic chemistry, they have not hitherto been noted with conjugated systems, although it is possible that some reactions of tervalent nitrogen compounds and quadrivalent sulfur atoms may take place in the same manner.

The first step in the reaction in question is the formation of a 1,4-addition compound. In this compound the chlorine atoms are more reactive than

in phosphorus trichloride and it behaves more like phosphorus pentachloride. With acetic acid the compound forms at once the phosphonic acid and acetyl chloride just as phosphorus pentachloride gives phosphoric acid and acetyl chloride. With acetic anhydride, the acid chloride II is produced. In glacial acetic acid this same intermediate compound is probably first formed and then the phosphorus oxygen ring is opened by the acetic acid or some hydrogen chloride which is always produced in small amounts.

Like many primary addition compounds, this addition compound is unstable and easily reverts to its factors. If the unsaturated ketone and phosphorus trichloride are mixed together and then treated with water, only a trace of the keto-phosphonic acid is produced. With a reagent like acetic acid or anhydride, however, the addition compound can react faster than the phosphorus trichloride, and *under these conditions* the reaction goes to completion. It will be shown in a subsequent paper that in the case of saturated aldehydes and ketones a 1,2-addition compound is formed, but in this case the intermediate product is more stable and larger yields of the phosphonic acid can be obtained by the direct treatment with water.

II. Experimental.

Reaction in Glacial Acetic Acid.

The keto-phosphonic acids described in the preliminary paper¹ were prepared by allowing the reaction to proceed in glacial acetic acid and then pouring into water. In this way very good yields of phosphonic acids were obtained from benzal-acetophenone, anisal-acetophenone, and dibenzal-acetone. It has now been possible to show that the phosphonic acid and acetyl chloride are formed before the treatment with water. The phosphonic acid may be thrown out of the acetic acid solution by dilution with an inert solvent like benzene.

Five grams of anisal-acetophenone was dissolved in 5 g. of acetic acid, 10 cc. of benzene and 4 g. of phosphorus trichloride. After standing 4 hours the clear solution was diluted with 50 cc. of benzene and seeded with the phosphonic acid. Crystallization immediately started and at the end of 48 hours, 4 g. of phosphonic acid was obtained (60% of the calculated amount).

Acetyl chloride was identified as the other product of the reaction by carrying out a similar experiment omitting the benzene. A simple distillation yielded acetyl chloride which was identified by redistillation and its reactions with water and aniline.

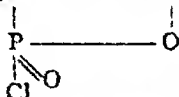
Reaction in Acetic Anhydride.

Acetic anhydride and phosphorus trichloride do not react at room temperature. When an unsaturated ketone is added, however, a reaction takes place with the evolution of considerable heat and is complete in about

¹ *Loc. cit.*

30 minutes. On pouring into water the phosphonic acid is obtained. If the reaction mixture is evaporated under diminished pressure, an oil is obtained which is a mixture of the acid chloride and the acid anhydride described in the introduction. These substances are very sensitive to moisture, and very dry reagents must be used throughout the work, and precautions must be taken to prevent the entrance of moist air. The compounds also must not be heated to too high a temperature and the evaporation *in vacuo* must, therefore, be carried out below 80°. If one molecule of acetic anhydride is used for every molecule of phosphorus trichloride, the oil obtained is almost wholly the acid chloride. A typical experiment is as follows

Ten grams (0.05 g. mol.) of benzal-acetophenone (dried over phosphorus pentoxide) was introduced into a mixture of 7 g. (0.05 g. mol.) of phosphorus trichloride and 5 g. of acetic anhydride (0.05 g. mol.). (The anhydride was purified by heating with phosphorus pentachloride and pentoxide and then carefully fractionating.) The reaction mixture was agitated from time to time and the temperature kept below 35°. At the end of one hour the volatile material was evaporated under diminished pressure in a stream of dry air. The material was heated in a water bath kept at about 70°. After 2 hours a thick, light colored oil was left behind. This was the crude acid chloride, $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{C}(\text{Cl})(\text{O})-\text{C}_6\text{H}_5$. It was



dissolved in dry chloroform and the solution made up with more chloroform to a known volume. A one-cc. portion was then shaken with 50 cc. of water and the chloride ion in the aqueous layer was determined by the Volhard method. The total active chlorine in the entire material could then be calculated.

Calc. for acid chloride 0.050 equivalents of chlorine Found 0.049.

The acidity of the aqueous layer was also determined. It was somewhat greater than the theoretical because of the slight solubility of the phosphonic acid.

Calc. for 1 HCl 0.050 equivalents. Found 0.057.

By using larger amounts of acetic anhydride and proceeding in exactly the same way, products could be obtained which contained much less of the acid chloride and more of the acid anhydride as shown by the amount of active chlorine. Ten grams of ketone, 7 g. of phosphorus trichloride and 15 g. of acetic anhydride (3 mol.) were treated as in the former experiment. The oil was dissolved in chloroform and a sample of the solution shaken with water and the aqueous layer analyzed.

Calc. for acid chloride 0.050 equivalents of chlorine. Found: 0.012.

The mixture thus contains only about 25% of the acid chloride. Such results are, of course, only approximate as small amounts of acetyl chloride and phosphorus trichloride which might be held by the oil would tend to vitiate them.

Reactions of the Acid Chloride and Acid Anhydride.

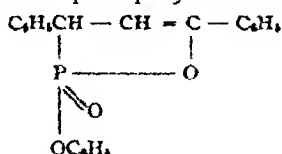
(a) **With Water.**—The oil obtained as just described was soluble in chloroform, carbon tetrachloride and benzene, but could not be made to crystallize, nor could it be distilled. Both the oil and its solutions energetically combine with water forming the phosphonic acid.

For example, 10 g. of benzal-acetophenone, 7 g. of phosphorus trichloride and 5 g. of acetic anhydride (equivalent quantities) were allowed to react and the product treated as described. The oil was dissolved in 25 cc. of dry carbon tetrachloride and 0.9 cc. of water (one mol.) was added. The drops of water soon disappeared completely and the temperature of the solution rose from 20° to 35°; a little hydrogen chloride was evolved. The solution was now shaken with 50 cc. of water and the carbon tetrachloride layer separated. Before the separation was finished, the phosphonic acid began to separate and was filtered off. The carbon tetrachloride was evaporated to dryness and the entire crude phosphonic acid was recrystallized from dilute alcohol solution, 11.5 g. of acid was thus obtained which was 78% of the theoretical amount.

In another parallel experiment in which 3 mols. of acetic anhydride was employed, a yield of 83% of phosphonic acid was obtained.

(b) **With Bromine.**—The oil obtained from 10 g. of benzal-acetophenone, 7 g. of phosphorus trichloride, and 5 g. of acetic anhydride (one mol.) was dissolved in dry carbon tetrachloride. A solution of bromine in the same solvent was slowly added. The bromine immediately disappeared and some heat was produced but no hydrogen bromide was evolved. When $\frac{1}{4}$ equivalent of bromine had been added, a slight red color was apparent for a few minutes, but quickly faded. A permanent red color was produced only when a little less than one molecule of bromine had been added. In previous experiments attempts to isolate a solid dibromide had failed, so that the transformation with water was studied. A few drops of water when added to the solution quickly disappeared and the temperature rose 10°. The solution was then shaken with 50 cc. of water and the layers separated. Thirteen grams of the monobromo-phosphonic acid described below (m. p. 197–198°) was obtained from the carbon tetrachloride layer. (80% of the theoretical amount.) The aqueous layer was analyzed for bromide ion by titrating with standard chlorine water and 0.046 equivalent was found; 0.050 equivalents would have been present if exactly one molecule of hydrogen bromide had been liberated in the process. The identity of the monobromo-phosphonic acid was shown by mixed melting-point determinations.

(c) **With Phenol.**—The oil obtained from 10 g. of benzal-acetophenone, 7 g. of phosphorus trichloride and 5 g. of acetic anhydride was dissolved in chloroform and 4.5 g. of phenol (1 mol.) was added. The solution was evaporated under diminished pressure and then heated for 20 min. at 125°; some hydrogen chloride was evolved. The material was dissolved in ether and extracted with sodium hydrogen carbonate solution. On acidification this yielded 7 g. of the monophenyl ester, m. p. 146°. The ethereal solution was dried and evaporated to dryness; it yielded 7 g. of an oil which was shown to be principally the compound,



This substance is insoluble in cold sodium carbonate solution and aqueous sodium hydroxide. It is soluble in alcoholic sodium hydroxide and on acidification the monophenyl ester is obtained. Some of the compound was heated to 125° for 10 minutes and hydrogen chloride bubbled through it. On treatment with water the monophenyl ester, m. p. 146°, was obtained. The phosphorus-oxygen ring is thus evidently opened by cold alcoholic sodium hydroxide and also by hydrogen chloride at a higher temperature.

The reaction with bromine definitely establishes the nature of the compound. Two grams of it was dissolved in chloroform and treated with bromine. A little less than one molecule was taken up by the solution before a permanent red color resulted; no hydrogen bromide was evolved. The solution was then shaken with water and from the chloroform layer there was obtained 1 g. of β -bromo-monophenyl ester, m. p. 176° (described below).

It is thus evident that the acid chloride and acid anhydride in question react with phenol at 125° and produce 2 substances: (1) the monophenyl ester acid, m. p. 146°, the ring probably having been opened by some hydrogen chloride; and (2) the phenyl ester of the cyclic acid. The intermediate compound used for this reaction was made with only one equivalent of acetic anhydride. It was thus almost wholly the acid chloride and it is very probable that this substance alone was involved in the reaction with phenol.

α -Phenyl- β -bromo- β -benzoyl-ethyl-phosphonic acid, $\text{C}_6\text{H}_5\text{CH}(\text{PO}_2\text{H})\text{CHBrCOC}_6\text{H}_5$.—The unsubstituted keto-phosphonic acid was prepared from benzal-acetophenone as described in an earlier paper.¹ 4.5 g. of this acid was dried at 130° and the resulting oil dissolved in chloroform. 2.3 g. of bromine in chloroform solution was added little by little. The reaction

¹ *Loc. cit.*

was started by heating for a few minutes on the steam bath. Hydrogen bromide was evolved and the bromine color rapidly disappeared until the equivalent amount of bromine had been added. The chloroform was removed by distillation under diminished pressure and the residual solid recrystallized from chloroform and petroleum ether. 3.5 g. of a white crystalline solid was thus obtained which melted at 196° . It could be recrystallized from a mixture of chloroform and petroleum ether or an alcohol-acetone solution.

The monobromo acid was very slightly soluble in water. The aqueous solution slowly became milky on standing and rapidly on heating. When treated with sodium hydrogen carbonate, sodium carbonate, or hydroxide, the monobromo acid was immediately transformed into benzal-acetophenone (an insoluble precipitate), sodium bromide and sodium phosphate. The reaction was almost quantitative. The phosphorus was to some extent eliminated from the molecule as a metaphosphate, as the solution gave the characteristic tests for this ion as well as for the orthophosphate ion.

Monophenyl ester of α -Phenyl- β -bromo- β -benzoyl-ethyl-phosphonic acid, $C_6H_5COCHBrCH(C_6H_5)PO(OH)(OC_6H_5)$.—This compound can be prepared from the bromo acid by first forming the acid chloride. Three grams of the bromo-phosphonic acid was dissolved in chloroform, 1 g. of thionyl chloride added and the mixture heated to 100° for half an hour; hydrogen chloride and sulfur dioxide were evolved. 0.8 g. of phenol was then added, the chloroform boiled off, and the heating continued for another half hour. The mixture was taken up in ether and 2.5 g. of the bromo ester acid slowly crystallized from the solution. The melting point was 179° . Titration with a standard base showed the substance to be a monobasic acid.

Calc. for $C_{21}H_{19}O_3PBr$ Br, 17.9 Found 17.8

The constitution of this substance follows from its formation from α -bromo-benzal-acetophenone. This latter compound was prepared in the usual way from benzalacetophenone dibromide.¹ Three grams of the α -bromo-benzal-acetophenone and 2.5 g. of phosphorus trichloride were dissolved in 10 cc. of glacial acetic acid. The mixture was allowed to stand overnight and then the volatile materials were removed by distillation under reduced pressure. The residue, taken up in chloroform, was heated for an hour at 100° with 1 g. of thionyl chloride; 0.9 g. of phenol was then added in chloroform solution and the heating continued for 30 minutes, the solvent being allowed to distil off at the same time. The resulting oil was treated with sodium hydrogen carbonate solution, a small amount of insoluble oil was removed, and the solution acidified. The material thus obtained was contaminated by a small amount of oil which was removed by again dissolving in sodium hydrogen carbonate and extracting

¹ *Am. Chem. J.*, 33, 38 (1903); 44, 323 (1910).

with ether. On precipitating with acid a material was obtained which could be crystallized from ether. Half a gram of the solid bromo-phenyl ester, m. p. 179° , was thus obtained and the identity of it and the product previously prepared was shown by making a mixed melting-point determination.

This bromo-monophenyl ester can be recrystallized from alcohol, since it is fairly soluble in the latter solvent. It dissolves in sodium hydrogen carbonate and carbonate solutions and the sodium salt may be prepared by cautious treatment with cold dil. sodium hydroxide solution. When warmed with sodium hydroxide or sodium carbonate solution it is decomposed in the same manner as the bromo acid and produces benzal-acetophenone.

Monophenyl ester of α -Phenyl- β -benzoylethyl-phosphonic acid, $C_6H_5COCH_2CH(C_6H_5)PO(OH)(OC_6H_5)$.—The bromo-monophenyl ester just described can be prepared by bromination of the unsubstituted monophenyl ester in chloroform solution. This latter substance can be prepared from the phosphonic acid by using only one mol. of thionyl chloride and heating the product with phenol. 10 g. of the keto-phosphonic acid was dehydrated by heating to 125° . The resulting oil was dissolved in chloroform and 5 g. of thionyl chloride was added. The chloroform was evaporated off and the oil heated to 140° in an oil bath. 3.5 g. of phenol was then added in chloroform solution and after evaporation of the chloroform, the mixture was heated to 135° for 20 minutes. The material was then dissolved in chloroform and extracted with sodium carbonate solution. Acidification yielded a solid which was recrystallized from alcohol. Yield, 7.5 g. of a crystalline substance melting at 146° . The chloroform solution contained a small amount of the diphenyl ester.

Calc for $C_{17}H_{19}O_4P$ C, 68.8, H, 5.2 Found C, 68.9, H, 5.6

Titration with standard sodium hydroxide solution using phenolphthalein as the indicator, showed the compound was a monobasic acid.

The most convenient method of preparing the bromo-monophenyl ester is from this ester; 3.5 g. of the ester was brominated in chloroform solution at the boiling point of the solvent. The chloroform was evaporated and the solid residue recrystallized from alcohol. Three grams was thus obtained melting at 179° .

Diphenyl Ester of α -Phenyl- β -benzoylethyl-phosphonic acid, $C_6H_5COCH_2CH(C_6H_5)PO(OC_6H_5)_2$.—This ester is obtained in small amounts when the monophenyl ester is prepared by the procedure just mentioned. It can be prepared in better yields by using 2 molecules of the thionyl chloride and then heating with 2 molecules of phenol. Thirty grams of the anhydrous phosphonic acid was dissolved in chloroform and heated with 10 g. of thionyl chloride for one hour at 100° ; 36 g. of phenol was added in

chloroform solution, the chloroform was distilled off and the mixture heated for 2 hours at 150°. The oily product was dissolved in ether and washed with sodium carbonate solution, and then with 5% sodium hydroxide solution to remove any phenol. On evaporating the ethereal solution a crystalline solid was obtained which was recrystallized from alcohol. Fourteen grams was thus obtained, which melted at 125°. Some monophenyl ester was obtained from the sodium carbonate solution.

Calc. for $C_{17}H_{15}O_2P$ C, 73.3, H, 5.2 Found C, 73.9; H, 5.3

This diphenyl ester can be readily hydrolyzed to the monophenyl ester in the following way. Six grams was dissolved in a solution of sodium alcoholate made from 0.3 g. of metallic sodium and 15 cc. of alcohol. After standing a few minutes the solution was poured into aqueous acid and the solid precipitate filtered off. This was purified by dissolving in sodium carbonate solution reprecipitating with acid and finally crystallizing from alcohol. Four grams of the monophenyl ester was thus obtained, melting at 146°.

Both the diphenyl ester and the monophenyl ester are hydrolyzed to the free phosphonic acid by warming with aqueous sodium hydroxide

Summary.

1. α,β -Unsaturated ketones react with phosphorus trichloride in glacial acetic acid producing a keto-phosphonic acid and acetyl chloride.

2. In acetic anhydride solution the product is a mixture of an unsaturated acid chloride and acid anhydride which have a phosphorus-oxygen ring. These substances readily react with water forming the keto-phosphonic acid.

3. The structure of the acid chloride and anhydride follows from the fact that they combine with one equivalent of bromine and the product with water gives a β -bromoketo-phosphonic acid. This β -bromo acid was synthesized by a method which proves its structure.

4. Additional evidence of the structure of the acid chloride and anhydride is afforded by a study of the products formed by heating it with phenol.

5. The structure of the compounds formed in acetic anhydride solution shows that the first step in the reaction is the addition of the phosphorus atom of the phosphorus trichloride to the ends of the conjugated system. Such an addition reaction involving the increase of valence of one atom is a new type of 1,4 addition.

CAMBRIDGE, MASS

[CONTRIBUTION FROM THE ANIMAL PHYSIOLOGICAL CHEMICAL LABORATORY, BUREAU OF CHEMISTRY, U S DEPARTMENT OF AGRICULTURE]

THE FOOD OF THE SMALL SEA HERRING AND AMMONIA AND AMINES AS END PRODUCTS OF ITS DECOMPOSITION.

BY F C WEBER AND J B WILSON

Received January 26, 1920

On the Atlantic Coast of the United States, canned sardines are prepared entirely from the sea herring (*Clupea harengus*). With the exception of a few canneries in Massachusetts, the industry is located in the State of Maine, the principal center of the industry being the towns of Eastport and Lubec, which lie at the entrance to Passamaquoddy Bay.

In the investigation of the sardine industry of Maine, conducted by the Animal Physiological Chemical Laboratory during the seasons of 1913 to 1916, decomposing food in the alimentary tract of these small fish was found to be one of the most important factors in rendering them unsuitable for packing. The term "feedy" is applied to those fish which have undigested and partly digested food remaining in the alimentary tract when caught. "Feedy" fish is one of the most troublesome factors in the sardine industry. Fish more or less gorged with food when taken from the water deteriorate very rapidly whereas those having their digestive tracts free from food when taken from the water remain in good condition for a comparatively long time. The rate of deterioration depends upon the quantity and stage of digestion of the food material contained in the digestive tract and the bacteria accompanying it. Food recently eaten and present in the stomach of the fish appears to cause a greater degree of deterioration than that which has been partially digested. In confirmation of this, bacteriological studies¹ showed that the stomach portions of the digestive tract were sterile when free from feed, though digestion was incomplete in the intestines. By the time "feedy" fish which have been 3 to 6 hours out of water reach the cannery, they have deteriorated to such an extent and are so badly broken that a large percentage is entirely unfit for packing.

The physical evidence of this deterioration is plainly seen by the ruptures of the stomach walls in earlier stages and later in the rupture and sloughing away of the belly portion of the fish. Fish brought to the canneries in such condition are termed "belly broken" or "belly-blown."

Food of the Sea Herring.

The young herrings from which sardines are made, constantly rove the seas in search of food. A plentiful supply of these fish, therefore, can

¹ The bacteriological work was done by M. M. Obst, Bacteriological Chemist, Microbiological Laboratory, Bureau of Chemistry, Washington, D C. A discussion of this work may be found in the *J. Infect. Dis.*, [2] 24, 158 (1910).

always be found in regions where food abounds, as the Passamaquoddy Bay region, where the largest number of sardine canneries have been built.

A number of observers, Moore,¹ Scott,² Hanson,³ Wheeler,⁴ MacDonald,⁵ Wright,⁶ and Bigelow,⁷ have explored the Atlantic Coast waters and have shown that the herring live chiefly upon minute crustaceans. Of these the chief forms are copepods, amphipods, schizopods, also the embryos of gasteropods and lamellibranchs.

The schizopods collected and used in this investigation were *Meganyctiphanes norvegica* (M. Sars). The copepods were identified by the U. S. National museum as mostly *Calanus finmarchicus* with smaller numbers of *Pseudocalanus elongatus* and *Temora longicornis*. These undoubtedly are the chief food of the herring of the Passamaquoddy Bay region. Fish which have been feeding extensively on either of the 2 kinds of food known to the fisherman as "red feed" and "shrimp" may be designated as "feedy" fish, which are most unsuitable for packing.

Examination of the Feed.

In order to determine the cause and the products formed in the decomposition of "feedy" fish, both the fish and the feed were subjected to chemical and bacteriological examination. Through the courtesy of the Bureau of Fisheries the authors were able to collect a sample of plankton at the Biological Station at Woods Hole, Massachusetts. The determinations made on this sample are recorded in the results of the chemical analyses. All other samples were obtained from the waters of Passamaquoddy Bay, off Eastport, Maine.

Collection of Samples.

Plankton.—The sample of plankton, taken at Woods Hole, Massachusetts, was obtained by tying a net made of bolting cloth just off the wharf at a point where a tidal current would run through it. About 4 hours later, and after the tide had begun to slacken, the net was brought in. The contents of the net were washed into a bolting cloth sieve with sea water, cleansed from seaweed and other foreign material then shaken

¹ H. F. Moore, "Observations upon the Herring and Herring Fisheries of the Northeast Coast, with special reference to the vicinity of Passamaquoddy Bay." U. S. Commissioner of Fish and Fisheries Report, 1896.

² Scott, "Observations on the Food of Fishes" 30th Ann. Rept. Fishery Board of Scotland, 1901, Pt. 3, 486-541.

³ H. H. Hanson, Proc. 8th Intern. Cong. Appl. Chem., 18, 131 (1912).

⁴ W. M. Wheeler, "The Free Swimming Copepods of the Woods Hole Region," U. S. Commission of Fish and Fisheries Bulletin, 1899.

⁵ D. I. MacDonald, Contributions to Canadian Biology, 1906-10, 83.

⁶ "The Plankton of Eastern Nova Scotia Waters," Contributions to Canadian Biology, 39th Ann. Rep. Dept. Marine and Fisheries, Fisheries Branch, Ottawa, Canada, 1907.

⁷ H. B. Bigelow, Bull. Museum Comp. Zool., Harvard University, 59, No. 4.

until practically all the water was removed. This sample was transferred to a glass bottle, and kept at the temperature of the laboratory until after the second analysis was made. The samples of plankton taken at Eastport, Maine, were obtained by the method employed for copepods.

Copepods (Feed or "Red Feed").—A net about 3 meters long, 1.23 meters in diameter at one end, and tapering to about 15 cm. in diameter at the other end, was used. The first 1.2 meters of the net consisted of coarse scrim; the remaining portion was of bolting cloth. A sterile Mason jar was fastened to the smaller end by means of a draw-string, and the net attached to the stern of the launch by a strong line. About 60 meters of rope was let out, and the net was dragged through the water at a depth ranging from 3 to 9 meters, just fast enough to keep the rope taut. Occasionally the net was brought in, the contents of the jar were transferred to another sterile jar, and the water was drained off. At the laboratory the sample was dried by shaking in a sieve of sterile bolting cloth, transferred to another sterile jar, and mixed for use.

Schizopods (Shrimp).—The schizopods were caught just as the tide began to go out, from a tender, among the rocks, behind breakwaters and other places more or less protected from the waves, by means of a small scrim scoop net, fitted with a long handle, and having an opening at the small end to which was fastened, by a draw-string, a sterile Mason jar. They were transferred to another sterile jar, and brought in sea water to the laboratory, where the water was drained off as completely as possible, the sample ground in an Enterprise meat grinder, and transferred to a sterile jar for use.

Feed from "Belly-Blown" Fish.—The stomach of each fish was removed with sterile instruments, slit with a scalpel, and the feed transferred to a sterile jar by means of a pair of tweezers previously sterilized in the flame.

Preparation of Samples.

With the exception of the plankton taken at Woods Hole, all the samples, during the intervals between analyses, were kept in an incubator at 37.5° at periods of time noted. Immediately after the preparation of the sample, samples for the determination of total volatile nitrogen and amines were removed by means of a sterile spatula, care being taken that the sample was not contaminated by material from the outside. At the end of each interval of time noted the material was removed from the incubator just long enough to weigh out the samples, and returned at once. The samples were placed in sterile jars and handled under aseptic conditions in order that they could also be used for bacteriological work.

Methods of Analysis.

Only the total volatile alkaline material, ammonia and total amines was determined in this investigation. At the time these studies were made—

the method for the separation of the amine fraction of the total volatile material had not been perfected. These methods have been reported in detail¹ in connection with a study of the formation of ammonia and amines in canned sardines.

As a result of the bacteriological work it was found that 2 organisms were associated with the feed (copepods and shrimp) of the small herring. One of these so closely resembles *Bacillus Walfischrauschbrand* that it has been so designated, and the other has been tentatively designated as *Bacillus B*. *Bacillus Walfischrauschbrand* is the name applied by Nielsen² to the organism found in diseased whales. *Bacillus Walfischrauschbrand* was also found to be responsible for the "swelling" of canned sardines. In fact, these organisms were first isolated from "swells," and later trace to the fish, where they were found upon the gills and in the intestinal tract with the feed.

The bacteriological examination of the feed showed that the bacterium (*Bacillus B*.) commonly associated with copepods grows faster and produces a slightly greater amount of gas than the organism *Bacillus Walfischrauschbrand* found chiefly on the shrimp.

In the French sardine industry³ bait is employed in the catching of the fish. So particular are the fisherman and the manufacturers to avoid the decomposition caused when fish are "feedy" that the strictest attention is given to the quality of the bait. In early times in this industry, owing to decomposition caused in the fish, the use of a prepared bait containing especially powdered prawn and shrimp was forbidden by royal decree. In this connection it is interesting to note that *Bacillus Walfischrauschbrand* found most commonly in shrimp is capable of decomposing fish tissue. This organism forms spores which are resistant to drying, but which are capable of growth and reproduction when conditions again become favorable. The bait prepared from dried shrimp doubtless contained the spores of this organism (*Bacillus Walfischrauschbrand*) which were responsible for the decomposition of the fish when this bait was employed.

In addition to the analyses made to determine the volatile alkaline constituents formed when the feed (copepods and schizopods—shrimp) was allowed to decompose, the same determinations were made upon culture media of the *Bacillus Walfischrauschbrand* and *Bacillus B*. When these bacteria were grown in pure cultures.

¹ F. C. Weber and J. B. Wilson, "The Formation of Ammonia and Amines in Canned Sardines During Storage." *J. Ind. Eng. Chem.*, 21, 121 (1919).

² Ivar Nielsen, "Ein Stück Moderner Bakteriologie aus dem 12. Jahrhundert," *Centr. Bakt. Parasitenk.*, 7, 267 (1890).

³ Hugh M. Smith, "French Sardine Industry," *U. S. Fish Commission Bull.* 1901, 9-10.

Composition of Copepods.

In an investigation of the chemical composition of plankton, Brandt¹ reports the analysis of material which consisted almost entirely of copepods as follows:

TABLE I.
Chemical Composition of Copepods (dry basis).

	%
Protein	58.80
Fat	7.40
Carbohydrates (by difference)	22.88
Ash	10.92
Composition of ash.	
SiO ₂	2.31
NaCl	1.49
Other salts	7.12

The composition of the dry substance of copepods, secured in the investigation made by Brandt, and which included varieties taken from fresh water, averaged as follows

TABLE II
Average composition of Copepods (dry basis)

	%
Protein	59.0
Chitin	4.7
Fat	7.0
Carbohydrates	20.0
Ash	9.3

Table III shows the results of the determination of ammonia and amines, as products of the decomposition of the feed of the herring, when the feed, copepods and schizopods (shrimp), were allowed to decompose under the most favorable conditions. The determination of the total volatile alkaline material in a catch of plankton, which consisted almost entirely of diatoms, taken at Woods Hole, Massachusetts, is also given. In all cases as many determinations were made on each sample as was possible with the amount of material obtained, which was not often large, as it was difficult to obtain any kind of feed except when the water was very quiet. The amount of total volatile nitrogen found before incubation was so small that it was not considered necessary to determine amine nitrogen.

Both ammonia and amines in very large quantities were found in the decomposing feed (schizopods and copepods). When allowed to spoil under these conditions and to the extent that took place during a period of 48 to 72 hours, ammonia was found in much larger amounts than amine.

¹ K. Brandt, Beiträge zur Kenntnis der Chemischen Zusammensetzung des Planktons. Wissenschaftliche Meeresuntersuchungen herausgegeben von der Kommission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel. Abt. Kiel Bd., 3, 43-90 (1898).

TABLE III.—AMMONIA AND AMINES IN SAMPLES OF FEED KEPT AT INCUBATOR TEMPERATURE (37.5°).¹

Sample No.	Description	Volatile nitrogen per 100 g.									
		When taken.		24 hrs in incubator		48 hrs in incubator		72 hrs in incubator			
		Am- Mg	Amines Mg	Am- Mg	Total Mg	Amines Mg	Total Mg	Am- Mg	Total Mg	Amines Mg	Total Mg
1	Plankton from Woods Hole, Mass., kept at 30°. Sample mostly composed of diatoms	2 82	4.14
3	Plankton from St. Croix River, off Campobello Island. Mostly composed of copepods	6 04
7	Copepods from east and south of Campobello Island	402.2
13	Copepods from shallow water east of Grand Manan Island	3 94	..	272 4	406 2	66 2	468 2	375 1	93 1
18	Copepods from north end Grand Manan Island in very deep water	216 6	151 8	62 8
5	Schizopods from Wilson's Beach, off Campobello Island	9 50	..	191 7	141 4	48 3	296 8	260 9	35 9
14	Schizopods from Wilson's Beach, off Campobello Island	822 9	602 3
21	Feed taken from "belly-blown" fish at wharf, Eastport, Me.	3 95	..	220 4	88 2	132 2	787 6	573 7	213 9	1009 2	832 6
		37 7	17 1	20 6

¹ Through the courtesy of the United States National Museum the copepods composing the different samples examined were identified for us as follows:

Nos. 3 and 13 were identified as *Calanus finmarchicus* (Gunner).

No. 7 contained *Calanus finmarchicus* (Gunner) and *Pseudocalanus elongatus* (Boeck) in about equal numbers.

No. 18, *Pseudocalanus elongatus* (Boeck) with a very few *Calanus finmarchicus* (Gunner).

Nos. 5 and 14 were identified as *Meganyctiphanes norvegica* (M. Sars).

From the number of determinations it was possible to make, it was apparent that little, if any, difference exists in the rate of decomposition or in materials formed between copepods and schizopods. Considering the similarity of composition of the two forms, it is quite probable that no difference in degree or kind of decomposition would be found. The examination of the feed taken from the viscera of "belly-blown" fish gave results confirming those found under artificial conditions. Both ammonia and amines were present in appreciable amounts, the quantity of amine in this instance being in excess of the ammonia.

Laboratory Experiments with *Bacillus Walfischrauschbrand* and *Bacillus B.*—To establish firmly the conclusion that the decomposition of the feed and of the fish, which results in the condition termed "belly-blown," is due to the presence of *Bacillus Walfischrauschbrand* and *Bacillus B.*, which were found in great numbers in the samples of feed and swelled cans examined, and to show that the presence of these bacteria is indicated by finding volatile nitrogen bases in "belly-blown" fish and swelled cans, these bacteria were grown in pure culture upon a medium containing fish protein, and the volatile alkaline products resulting from their growth determined. The fish used for preparing Cultures 24, 25, 31 and 32 (Table IV) were fresh Boston mackerel. Freshly caught Potomac bass were used for Cultures 27, 28, 29 and 30. After removing the skin, solid masses of meat were passed through a meat grinder and mixed with a solution of dextrose of such strength that the final mixture, of a uniform paste consistency, contained 0.2% of dextrose. The whole was then sterilized under 15 pounds pressure. Portions of this paste were inoculated with 24-hour dextrose agar anaerobic cultures of bacteria, and covered with an inch layer of sterilized fish broth made firm with 1.5% agar and no nutriment, and then incubated at 37.5° until removed for analysis. Whenever a sample was removed for analysis, the presence of the bacterium with which it has been inoculated was determined positively. The determinations are reported in Table IV.

The results show that both ammonia and amines are formed when *Bacillus Walfischrauschbrand* and *Bacillus B.* are grown in pure cultures on fish media. Under the conditions which obtained when these experiments were made, amines are formed in smaller amounts than when the different lots of feed are decomposed at incubator temperature. It would appear that a larger proportion of amines are formed during the decomposition of the feed and the fish under natural conditions. In the cultures of *Bacillus Walfischrauschbrand* and *Bacillus B.* used for the determination of ammonia and amines, positive tests for both indole and skatole were obtained.

These results confirm those shown in Table III that ammonia and amines are produced by these organisms during the decomposition of the feed.

TABLE IV—DETERMINATION OF AMMONIA AND AMINES IN PURE CULTURES OF BACILLUS WOLFSCHEUSCHENBRAND AND BACILLUS B GROWN IN THE LABORATORY

Culture No.	Bacteria	Time of incubation, days.	Volatile nitrogen per 100 g.			Percentage of total volatile nitrogen		Nitrogen determined by the amino-acid method per 10 g. Mg	Alkalinity (0.05 N acid per 10 g.) Cc
			Total Mg	Ammonia Mg	Amines Mg	Ammonia %	Amines %		
30	Sterile	7	18.5					0.55	0.0
28	<i>B. Wolfscuschenbrand</i>	2	250.5	215.2	41.3	82.9	17.1	5.34	..
28		4						5.65	..
31		7	510.1	447.1	63.0	87.7	12.3	9.95	2.1
32		7	354.6	286.2	48.4	85.6	14.4	5.16	1.5
24		2	146.8						1.2
24	<i>B. B.</i>	4	208.4	160.3	48.1	76.9	23.1		1.9
25		3	159.1	127.7	31.4	80.3	19.7		
29		2	145.8	132.6	13.2	91.0	9.0	2.52	
27 ^a		2	225.2	198.8	26.4	88.2	11.8	5.07	
27		3						5.59	

^a These determinations made by the Van Slyke method and apparatus (D. Van Slyke, *J. Biol. Chem.*, 16, 121 (1913).^b A few micrococci in this culture

Conclusions.

The copepods and schizopods (shrimp) constitute the chief forms of feed of the small sea herring of the Passamaquoddy Bay region. Of the copepods *Calanus finmarchicus*, *Pseudocalanus elongatus*, and *Temora longicornis* appear to be the chief species found in this region, and may be classed as the "red feed," as distinguished from shrimp.

The results of the examinations made show that ammonia and amines are found in very appreciable quantities when the different forms of food decompose. These results also show with what rapidity and to what extent the food decomposed. When the 2 kinds of bacteria, so commonly found associated with the feed, are grown in pure culture it is shown that ammonia and amines are formed in the media.

Skatole and indole were also detected in the culture media on which these bacteria were grown. Ammonia and amines were also determined in the contents of the digestive tract of "belly-blown," feedy fish. The results show that the formation of ammonia and amines in the decomposing food is due to the action of the 2 bacteria always found associated with the 2 forms of food (copepods and schizopods), whether taken directly from the water or from the digestive tracts of the fish. This decomposition, also accompanied by the evolution of gas when *Bacillus B* is present, is responsible for the bursting of the bellies ("belly-blown") of "feedy" fish.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY UNIVERSITY OF PITTSBURGH.]

SOME DERIVATIVES OF 2,4-DINITRO-BENZALDEHYDE.¹

BY ALEXANDER LOWY AND BLAINE B. WESCOTT

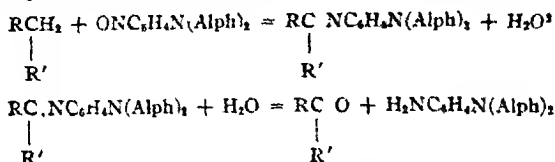
Received February 11, 1920

The work upon the derivatives of 2,4-dinitro-benzaldehyde was undertaken for the following reasons. (1) Upon examination, the literature revealed that relatively few derivatives of this compound have been prepared.² (2) Research upon trinitro-benzaldehyde was already under way in these laboratories and the results of this work, to be published in the near future, showed the desirability of a parallel investigation upon 2,4-dinitro benzaldehyde. (3) Since benzaldehyde has long been an important intermediate in the dye industry it seemed probable, reasoning by analogy, that 2,4-dinitro-benzaldehyde might also find considerable use in the manufacture of dyestuffs. (4) But perhaps the most im-

¹ This report represents a part of a thesis presented by Blaine B. Wescott in partial fulfillment of the requirements for the degree of Master of Science, January, 1920.

² *Ber.*, 35, 1224 (1902); *ibid.*, 35, 2703 (1902), *Monatsh.*, 23, 1003 (1902); *Ber.*, 37, 1861 (1904), *ibid.*, 39, 2754 (1906), *ibid.*, 40, 3230 (1907); *Monatsh.*, 23, 554 (1902); *Ber.*, 41, 109 (1908); *ibid.*, 42, 601 (1909); *J. prakt. Chem.*, 2, 89.

portant reason for the research upon this compound is the fact that it is a derivative of 2,4-dinitro-toluene, an important explosive, which is itself an intermediate in the manufacture of trinitro-toluene. It is evident that an outlet for the great stocks of 2,4-dinitro-toluene and trinitro-toluene now on hand is an economic necessity. Such an outlet was suggested in 2,4-dinitro-benzaldehyde and trinitro-benzaldehyde. The method used in the preparation of 2,4-dinitro-benzaldehyde was essentially that described by F. Sachs and R. Kempf.¹ They stated that the conversion of the methyl group of an aromatic compound to the aldehyde group is possible by a condensation with a nitroso-dialkyl-aniline and subsequent hydrolysis with mineral acids.



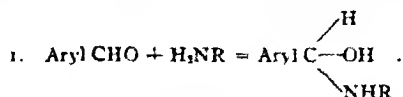
They found that the above reactions proceeded easily in the preparation of 2,4-dinitro-benzaldehyde and they described the following method for its production. 45 g. of 2,4-dinitro-toluene, 40 g. of nitroso-dimethylaniline, 75 g. of sodium carbonate (anhydrous crystals) and 250 cc. of 95% ethyl alcohol were heated together on a steam bath for 5 hours under a reflux condenser, with frequent shaking. After a time nearly the whole mixture solidified to a mass of green granules. After filtration, the residue was washed with several liters of hot water. The yield of the condensation product was 86%. The condensation product was then shaken with 250 cc. of 27% nitric acid and 250 cc. of benzene for some hours. The mixture was filtered and the benzene layer separated from the filtrate. After the benzene had been distilled, the residue, a dark oil which solidified on cooling, was dissolved in alcohol and boiled with animal charcoal. The charcoal was then filtered off and just enough water added to the filtrate to cause it to become cloudy. The aldehyde crystallized out upon standing in long, yellow needles which melted at 72°. Yield, 88%. Several difficulties were encountered at once in their process which necessitated considerable investigation. (1) A low yield, 25%, of the product was obtained. (2) Considerable quantities of oil adhered to the crystals. (3) 250 cc. of benzene was found to be an entirely inadequate amount for the complete extraction of the 2,4-dinitro-benzaldehyde.

The reactions carried out in the study of 2,4-dinitro-benzaldehyde were all of the general type known as condensations. The first type of condensation studied was that of the reaction between 2,4-dinitro-benzaldehyde

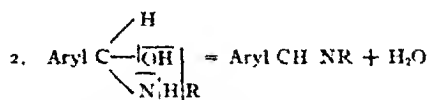
¹ *Ber.*, 35, 2704 (1902).

² *Ibid.*, 32, 2341 (1899); 33, 959 (1900); 34, 118, 498 (1901); 34, 3047 (1901).

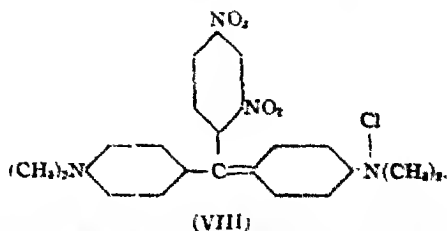
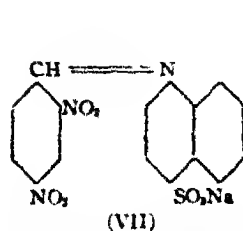
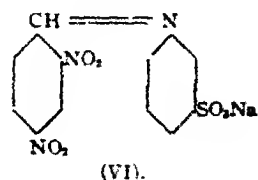
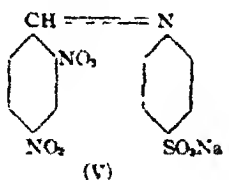
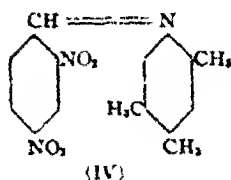
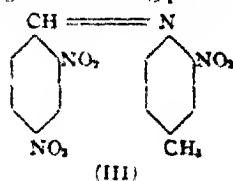
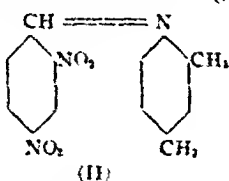
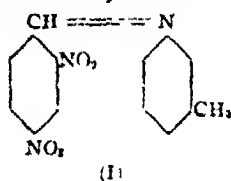
and different aromatic amines. The reaction is accompanied by the elimination of one molecule of water and may be expressed by the general type reaction, $\text{Aryl CHO} + \text{H}_2\text{NR} = \text{Aryl CH:NR} + \text{H}_2\text{O}$. The class of condensation products formed in reactions as typified by the above equation are known as "Schiff's bases."¹ The reaction proceeds in 2 stages: The first consists of the formation of an intermediate addition product,



The second consists of the splitting off of one molecule of water from the addition product,



The same type of reaction is possible with either substituted aldehydes or amines or both. Condensations were carried out between 2,4-dinitrobenzaldehyde and various substituted amines giving the following products:

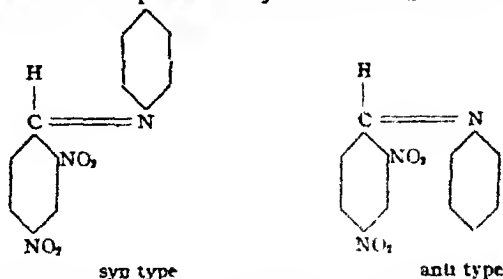


It is often impossible to isolate the intermediate addition product of the aldehyde-amine condensations due either to the instability of the compound or to the velocity of the second stage of the reaction. Although the isolation of the addition product in the condensation of 2,4-dinitro-

¹ *Ber.*, 35, 984 (1902).

benzaldehyde and aniline was attempted, the effort was not successful. More work upon this phase of the subject is to be undertaken at a later date.

The results of the work proceeding simultaneously upon trinitro-benzaldehyde, which will be published in the near future, suggested the possibility of the existence of the condensation products in 2 stereoisomeric forms. The 2 stereoisomeric forms of the 2,4-dinitro-benzylidene-aniline would be represented by the following formulas.



However, no evidence of the existence of 2 stereoisomeric forms of any of the condensation products produced from 2,4-dinitro benzaldehyde was found.

The second type of condensation studied was that taking place in the reaction of one molecule of an aromatic aldehyde and 2 molecules of a tertiary alkylaniline in the presence of a condensing agent such as anhydrous zinc chloride, or conc. hydrochloric acid. This type of condensation was used to obtain 2,4-dinitro-tetramethyl-diamino-triphenyl-methane. The reactions were analogous to those used to produce malachite green. The experiments were of a qualitative nature only but the quantitative results are to be worked out and published in a later paper. The dye as prepared in the preliminary trials dyed silk a greenish blue shade, very much like that produced by malachite green.

Experimental Part.

Preparation of 2,4-Dinitro-benzaldehyde.—The following method for the preparation of 2,4-dinitro-benzaldehyde was finally adopted after considerable investigation. 100 g. of 2,4-dinitrotoluene, 89 g. of nitroso-dimethylaniline, 167 g. of sodium carbonate and 555 cc. of alcohol were heated for 5 hours on a steam bath under a reflux condenser. The condensation product was filtered free of alcohol and leached with acetic acid until the sodium carbonate was entirely decomposed, after which the mixture was filtered and the residue washed free of acetic acid with water. The condensation product was hydrolyzed by treatment with 250 cc. of 1:1 hydrochloric acid for 3 hours at 80° with mechanical stirring. The resulting mixture was extracted repeatedly with hot benzene. The small

amount of oily material from the acid layer which passed over into the benzene extract was removed by filtration. The benzene was then distilled off and the 2,4-dinitro-benzaldehyde recovered from the residue by repeated extraction with hot water. The water extract was separated from the oil by filtration through a hot-water funnel. The 2,4-dinitro-benzaldehyde separated from the filtrate in long, yellow needles upon cooling. The melting point of the 2,4-dinitro-benzaldehyde obtained by the above process was 71° . The identity of the product was further established by carrying out the condensation with aniline as described by Sachs and Kempf.¹

2,4-Dinitrobenzal-*m*-toluidine, $C_6H_3(NO_2)_2CH \cdot NC_6H_4(CH_3)$ (I).—This compound was prepared by adding 2.8 g. of *m*-toluidine to 5 g. of 2,4-dinitro-benzaldehyde dissolved in 25 cc. of glacial acetic acid. The condensation product separated almost immediately. The mixture was heated on a steam bath to insure the completion of the reaction. After 2 hours it was cooled, diluted with water, filtered and washed with dil. acetic acid and water. The product was purified by recrystallization from benzene. The purified substance crystallized in fine, yellow needles which melted at 130° . It was easily soluble in benzene, chloroform, acetic acid and acetone slightly soluble in alcohol, and insoluble in water. Yield, 5.4 g. The product gave 2,4-dinitro-benzaldehyde upon hydrolysis with hot 1:1 hydrochloric acid.

Subs., 0.2000, 0.2050; 26.55 cc. N (18.6° , 742 mm.), 27.3 cc. N (20.5° , 744.5 mm.).

Calc. for $C_{12}H_9(NO_2)_2CH \cdot NC_6H_4(CH_3)$ N, 14.73. Found 14.89, 14.79.

2,4-Dinitrobenzal-1,3,4-xylylidine, $C_6H_3(NO_2)_2CH \cdot NC_6H_3(CH_3)_2$ (II).—This substance was prepared by adding 3 g. of 1,3,4-xylylidine to 5 g. of 2,4-dinitro-benzaldehyde dissolved in 25 cc. of glacial acetic acid after which the mixture was heated for 2 hours on a steam bath. It was then cooled, diluted with water, filtered and washed with dil. acetic acid and water. The product was purified by recrystallization from acetone. It formed long, deep yellow needles of a silky luster having a melting point of 210.5° . The compound is fairly soluble in benzene, acetone, chloroform and acetic acid, slightly soluble in alcohol and insoluble in water. Yield, 7 g. Upon hydrolysis with hot 1:1 hydrochloric acid it yielded 2,4-dinitro-benzaldehyde.

Subs., 0.2018, 0.2014, 0.2004, 25.38 cc. N (17.0° , 731.6 mm.), 25.7 cc. N (20.0° , 747.6 mm.), 25.9 cc. N (22.0° , 742 mm.).

Calc. for $C_{18}H_{11}(NO_2)_2CH \cdot NC_6H_3(CH_3)_2$ N, 14.04. Found 13.97, 14.27, 14.21.

2,4-Dinitrobenzal-3-nitro-4-toluidine, $C_6H_3(NO_2)_2CH \cdot NC_6H_3(NO_2)(CH_3)$ (III).—A solution of 4 g. of 3-nitro-4-toluidine in 50 cc. of glacial acetic acid was added to a solution of 5 g. of 2,4-dinitro-benzaldehyde in 50 cc. of glacial acetic acid. The mixture was heated for 2 hours on a steam

¹ Ber., 35, 1224 (1902).

bath after which it was evaporated until crystallization took place. Purification was accomplished by recrystallization from glacial acetic acid. The substance separated in radiating clusters of fine, light brownish yellow needles which had a melting point of 195° . The product was easily soluble in acetone, chloroform and glacial acetic acid, slightly soluble in alcohol and benzene and very slightly soluble in water. Yield, 3.2 g. Upon hydrolysis with hot 1:1 hydrochloric acid it yielded 2,4-dinitro-benzaldehyde.

Subs., 0.2008, 0.1196; 30.3 cc. N (19.5° , 739.7 mm.), 19 cc. N (23.5° , 731.8 mm.).

Calc. for $C_6H_3(NO_2)_2CH:NC_6H_3(NO_2)(CH_3)$: N, 16.96. Found: 16.75, 17.09.

2,4 - Dinitrobenzal - pseudocumidine, $C_6H_3(NO_2)_2CH:NC_6H_3(CH_3)_2$: (IV).—This substance was prepared by adding a solution of 2.3 g. of pseudocumidine dissolved in 25 cc. of glacial acetic acid to a solution of 3.4 g. of 2,4-dinitro-benzaldehyde dissolved in 75 cc. of glacial acetic acid. The condensation product separated immediately in a bright yellow mass. The mixture was heated for 2 hours on a steam bath after which it was diluted with water, filtered, washed with dil. acetic acid and water. The product was purified by recrystallization from benzene from which it separated in fine, bright yellow needles with a silky luster. The melting point of the compound was 186.5° . Yield, 4.4 g. The product was easily soluble in benzene, acetone, chloroform and acetic acid, slightly soluble in alcohol and ether, and insoluble in water. Upon hydrolysis with hot 1:1 hydrochloric acid it gave 2,4-dinitro-benzaldehyde.

Subs., 0.2022, 0.2017, 0.2018; 24.98 cc. N (19.0° , 733 mm.), 24.95 cc. N (20.0° , 735 mm.), 25.5 cc. N (22.0° , 730.7 mm.).

Calc. for $C_{12}H_7(NO_2)_4CH:NC_6H_3(CH_3)_2$: N, 13.42. Found: 13.62, 13.61, 13.68.

2,4-Dinitrobenzal-sodium Sulfanilate, $C_6H_3(NO_2)_2CH:NC_6H_4SO_3Na$. H_2O (V).—This product was prepared by adding 5 g. of 2,4-dinitrobenzaldehyde dissolved in 50 cc. of alcohol to 5 g. of sodium sulfanilate dissolved in 150 cc. of alcohol. The mixture was heated for 2 hours on a steam bath under a reflux condenser after which it was evaporated to crystallization. The mother liquor was filtered off and a further evaporation yielded more of the product. The compound was purified by recrystallization from 1:1 alcohol. It separated in very fine, pale yellow crystals, which decomposed at 249° . The product was easily soluble in water, and slightly soluble in alcohol, ether, benzene, acetone and chloroform. Yield, 8.2 g. Upon hydrolysis with hot 1:1 hydrochloric acid it gave 2,4-dinitro-benzaldehyde. The water of crystallization was determined by heating the air-dry product for 12 hours at 105° .

Subs. (air dry), 0.2120, 0.2930; loss, 0.0098, 0.0132 (12 hours at 105°).

Calc. for $C_{12}H_8N_2O_7SNa \cdot H_2O$, 4.60. Found: 4.62, 4.50.

Subs., 0.1683; $BaSO_4$, 0.0999.

Calc. for $C_{12}H_8N_2O_7SNa \cdot H_2O$: S, 8.20. Found: 8.15.

Subs., 0.2019, 0.2007; 19.5 cc. N (17.5° , 733 mm.), 19.85 cc. N (17.5° , 732.2 mm.).

Calc. for $C_{12}H_8N_2O_7SNa \cdot H_2O$: N, 10.73. Found: 10.73, 10.96.

2,4-Dinitrobenzal-sodium Metanilate, $C_6H_3(NO_2)_2CH.NC_4H_5SO_3Na.3H_2O$ (VI).—This compound was made by adding 5 g. of 2,4-dinitrobenzaldehyde dissolved in 50 cc. of alcohol to 5 g. of sodium metanilate dissolved in 250 cc. of alcohol. After $\frac{3}{4}$ of the alcohol had been evaporated the mixture was heated for 2 hours on a steam bath under a reflux condenser. It was evaporated to crystallization and a further amount of the product recovered from the mother liquor after filtration and further evaporation of the filtrate. The compound was purified by recrystallization from 1:1 alcohol from which it separated in very fine, deep yellow needles. The product decomposed at 185° . Yield, 5.4 g. The substance was soluble in water and slightly soluble in alcohol, chloroform, acetone and benzene. The water of crystallization was determined by heating the air-dry product for 12 hours at 105° .

Subs. (air-dry), 0.4617, 0.1896, 0.1514; loss, 0.0613, 0.0252, 0.0199 (12 hours at 105°).

Calc. for $C_{11}H_4N_2O_7SN_3.3H_2O$. H_2O , 12.65. Found: 13.28, 13.29, 13.14.

Subs. (dry), 0.2013, 0.2003, 21.8 cc. N (24.0° , 739.2 mm.), 21.9 cc. N (26.5° , 734.8 mm.).

Calc. for $C_{11}H_4N_2O_7SN_3.3H_2O$. N, 9.83. Found 10.24, 10.14.

Subs. (dry), 0.2049; $BaSO_4$, 0.1270.

Calc. for $C_{11}H_4N_2O_7SN_3.3H_2O$. S, 7.50. Found 7.43.

2,4-Dinitrobenzal-sodium Naphthionate, $C_6H_3(NO_2)_2CH.NC_{10}H_6SO_3Na.0.5H_2O$ (VII).—This substance was prepared by adding 5 g. of 2,4-dinitrobenzaldehyde dissolved in 50 cc. of alcohol to 6.3 g. of sodium naphthionate dissolved in 180 cc. of alcohol. After $\frac{1}{4}$ of the alcohol had been evaporated the mixture was heated for 2 hours on a steam bath under a reflux condenser. The product was obtained by the evaporation of the solution to crystallization. A further quantity was recovered by the evaporation of the mother liquor after filtration. The substance was purified by recrystallization from 1:1 alcohol from which it separated in very fine, bright orange needles which decomposed at 248° . Yield, 7.9 g. It was soluble in water and slightly soluble in alcohol, ether, benzene, chloroform and acetone. It yielded 2,4-dinitrobenzaldehyde upon hydrolysis with hot 1:1 hydrochloric acid. The water of crystallization was found by heating the air-dry product for 12 hours at 105° .

Subs. (air-dry), 0.3144, 0.1032; loss, 0.0062, 0.0018 (12 hours at 105°).

Calc. for $C_{17}H_{10}N_2O_7SN_3.0.5H_2O$. H_2O , 2.08. Found: 1.97, 1.79.

Subs. (dry), 0.1318; $BaSO_4$, 0.0762.

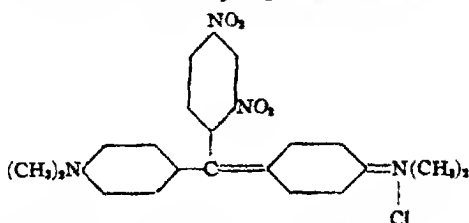
Calc. for $C_{17}H_{10}N_2O_7SN_3.0.5H_2O$. S, 7.42. Found: 7.76.

Subs., 0.2014, 0.2006; 18.6 cc. N (24.0° , 726 mm.), 17.65 cc. N (27.0° , 745.2 mm.).

Calc. for $C_{17}H_{10}N_2O_7SN_3.0.5H_2O$. N, 9.72. Found: 9.82, 9.95.

2,4-Dinitrobenzaldehyde-dimethylaniline Condensation. VIII.—This condensation which is analogous to that carried out in the preparation of malachite green was performed only in a qualitative way. The

directions given for the preparation of malachite green by Gattermann¹ were followed. The product obtained was a green powder which dyed silk a bluish green shade very similar to that produced by malachite green. The following formula undoubtedly represents the structure of the dye:



The quantitative results, as stated above, will be published in a later paper.

Summary.

1. The method described by Sachs and Kempf for the preparation of 2,4-dinitro-benzaldehyde was found to be unsatisfactory and a modified method for its preparation was worked out.
2. Eight derivatives of 2,4-dinitro-benzaldehyde were prepared and analyzed and certain physical properties and solubilities determined.
3. These compounds, like many other similar condensation products, are affected to a greater or less extent by the action of light.

PITTSBURGH, PENNA.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY. NO. 85]

A STUDY OF THE SULFUR DERIVATIVES OF BUTYL ALCOHOL.

BY H. LEB. GRAY AND GURNEY O. GUTKUNST

Received February 20, 1920

In the course of our work in this laboratory, it was necessary to prepare large quantities of butyl sulfone. This involved not only a complete study of the methods of preparation of the sulfone but of butyl sulfide as well.

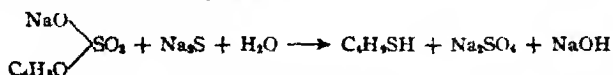
Grabowsky and Saytzeff² prepared butyl sulfide by heating an alcoholic solution of potassium sulfide with butyl iodide. A disadvantage of this method consists in the difficulty of preparing large quantities of alcoholic sodium or potassium sulfide so it was decided to prepare the butyl sulfide by distilling sodium sulfide with an aqueous solution of sodium butyl sulfate, the latter being prepared by the action of fuming sulfuric acid on butyl alcohol.

It was found that low yields were obtained by this method; this was

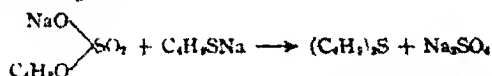
¹ "Practical Methods of Organic Chemistry."

² *Ann.*, 171, 251 (1874).

not due to a poor yield of butyl sulfuric acid, but to the formation of butyl mercaptan as well as butyl sulfide. This could not be attributed to the presence of large amounts of sodium hydrosulfide in the sodium sulfide since the mercaptan is formed even in the presence of a slight excess of sodium hydroxide. It has been found that sodium butyl sulfate when distilled with sodium sulfide in presence of water tends to form butyl mercaptan in the following manner



We found that butyl sulfide is satisfactorily formed when the mixture of sodium butyl sulfate and sodium sulfide is refluxed, but that things go wrong when the mixture is distilled without first refluxing. This looks like a case of mass action, since butyl mercaptan is removed as fast as it is formed, but reacts further if it is kept in the reaction mixture. It was also found that the addition of a large excess of sodium hydroxide materially diminishes the formation of mercaptan when the mixture is distilled direct without refluxing. This is undoubtedly due to the formation of the sodium salt of butyl mercaptan, which reacts with sodium butyl sulfate in the following manner



Grabowsky¹ prepared butyl sulfone by the action of fuming nitric acid on dibutyl sulfide. This method was thoroughly investigated and was finally discarded owing to the fact that a large excess of nitric acid is necessary and that the method is not dependable. The yield varied from 30% to 70% under apparently the same conditions, and great difficulty is experienced in purifying the product.

An attempt was made to oxidize the sulfide with nitrogen dioxide but was unsuccessful.

Oxidation with sodium permanganate was then tried and proved to be very successful. Excellent yields were obtained, and the product was quite pure.

During the course of these experiments butyl mercaptan was oxidized by means of potassium dichromate. A yellow oil resulted which boiled at 228–230° (uncorr.) and which we assumed to be *n*-dibutyl disulfide.

I. Butyl Sulfide.

From Butyl Alcohol.—350 g. of fuming sulfuric acid (20% sulfur trioxide) was gradually added to 1000 g. of butyl alcohol with constant stirring. The mixture was placed on the water bath and heated for 15 hours. It was then cooled and the excess acid was neutralized with a saturated solution

¹ *Ann.*, 175, 350 (1875).

of sodium carbonate, and the unchanged butyl alcohol distilled off. 690 g. of butyl alcohol was recovered. The use of sodium carbonate entirely in the place of lime eliminated 2 filtrations and does not affect the yield of butyl sulfide. The mixture was diluted to about 5 liters and slowly distilled with a solution of 217 g. ($\frac{1}{3}$ excess) of sodium sulfide, care being taken not to distil the sulfide too rapidly. The crude distillate was fractionated and yielded 107 g. (35%) of butyl sulfide and 61 g. of butyl mercaptan. It was thought that the small yield of sulfide might be due to a low yield of butyl sulfuric acid caused by the temperature of the reacting mixture being too low. The effect of refluxing at boiling temperature, the mixture of butyl alcohol and fuming sulfuric acid (20% sulfur trioxide) resulted in the formation of dibutyl ether.

Dibutyl Ether.—350 g. of fuming sulfuric acid was gradually added to 1000 g. of butyl alcohol as above. The mixture was boiled under a reflux condenser for 15 hours, cooled, neutralized with sodium carbonate solution, and the butyl alcohol distilled off. The residue was slowly distilled with 316 g. of sodium sulfide. Only 40 g. of butyl sulfide was obtained. The butyl alcohol distillate was fractionally distilled and yielded 400 g. of dibutyl ether, boiling sharply at 140° . This represents a yield of 45%. There is little doubt but that this method could be so developed that much larger yields of the ether could be obtained.

Action of Sodium Butyl Sulfate on Butyl Mercaptan in Presence of Sodium Hydroxide.—90 g. of butyl mercaptan and 176 g. of sodium butyl sulfate were mixed, made strongly alkaline with 40 g. of sodium hydroxide, and boiled under a reflux condenser for 3 hours. An oily layer separated. The reaction mixture was cooled, and the oil layer separated. This was dried over calcium chloride and fractionally distilled. 77 g. of pure butyl sulfide was obtained, representing a 53% yield.

Effect of Refluxing with Sodium Hydroxide Solution.—350 g. of fuming sulfuric acid was gradually added to 1000 g. of butyl alcohol with constant stirring and the mixture heated on the water bath for 15 hours. It was then neutralized with sodium carbonate, and the butyl alcohol distilled off. 636 g. of the alcohol was recovered. 261 g. of sodium sulfide and 200 g. of sodium hydroxide were dissolved in water and added to the reaction mixture. This was boiled under a reflux condenser for 3 hours and then slowly distilled. The crude sulfide was separated from the aqueous layer, dried and fractionally distilled. 266 g. (72 %) of butyl sulfide boiling between $180-185^{\circ}$ was obtained.

II. Butyl Sulfone.

Oxidation with Nitric Acid.—545 g. (40% excess) of fuming nitric acid (90%) was placed in a 3-liter round-bottom flask provided with a long reflux condenser, and heated to moderate boiling. 400 g. of butyl

sulfide was added drop by drop through the condenser. A vigorous reaction took place in the condenser tube. After all the sulfide was added, the contents of the flask were boiled until nitrogen dioxide fumes ceased to be evolved (about one hour). The reaction mixture was poured into an evaporating dish and as much nitric acid as possible evaporated off on the water bath. The crude mixture was dissolved in ether, neutralized with sodium carbonate, the ethereal layer separated, and the water solution extracted once with ether. The ether extracts were washed with water and combined. On evaporating off the ether, a yellow oil was obtained which solidified on cooling in an ice and salt mixture. This yellow solid was broken up and centrifuged. The butyl sulfone was obtained as yellow crystals. A yellow oil also resulted. After several recrystallizations from alcohol, the sulfone crystallized as pure white flakes which melted at 43.5° . Yield, 308 g. or 63% of pure butyl sulfone. No further separation of crystals resulted on cooling the yellow oil. This oil on distillation decomposed yielding butyl sulfide.

The yields obtained by this method varied from 10 to 63%, although the experiments were apparently conducted under exactly the same conditions. The method is unreliable and not to be depended upon as a source of butyl sulfone.

Oxidation with Nitrogen Dioxide.—An attempt was made to oxidize butyl sulfide to butyl sulfone by means of nitrogen dioxide. For this purpose, 200 g. of butyl sulfide was placed in a 500-cc. round-bottom flask, and the gas bubbled through slowly until no more heat was generated. The reaction mixture was neutralized with sodium carbonate and extracted with ether. On distilling off the ether and cooling the residue, a few crystals of butyl sulfone were obtained.

Oxidation with Sodium Permanganate.—400 g. of dibutyl sulfide was placed in an open earthenware vessel and stirred by means of an efficient stirrer. Technically pure sodium permanganate solution was added in small portions. A very vigorous reaction took place with separation of a large quantity of manganese dioxide. A 25% solution of sulfuric acid (equivalent to 163 g. of conc. acid) was added from time to time in quantities just sufficient to keep the mixture thin enough to admit of efficient stirring. The permanganate was added until no more heat was generated, about 300 g. being necessary. The reaction mixture was allowed to stand until the manganese dioxide had settled and an almost colorless oil separated on top. This oil was poured off. The residual manganese dioxide was extracted with ether and the oil resulting from the ether extract added to the first. The oil solidified to a light yellow crystalline mass on cooling in an ice and salt mixture. This crystalline mass was broken up and centrifuged, yielding practically pure butyl sulfone and a few g. of a light yellow oil. One crystallization from alcohol was sufficient

to obtain a pure product melting at 43.5° . A yield of 390 g., or 80%, resulted.

Summary.

1. It has been found that butyl mercaptan in comparatively large yields is obtained on distilling a solution of sodium sulfide with sodium butyl sulfate.

2. It has been shown that no butyl mercaptan is obtained when a large excess of sodium hydroxide is used

3. It has been found that butyl sulfide can be obtained by the interaction of butyl mercaptan and sodium butyl sulfate in the presence of sodium hydroxide.

4. A method for the preparation of dibutyl ether is given.

5. An improved method for preparing butyl sulfide has been described. Average yields of 72% can be obtained.

6. It has been found that the oxidation of butyl sulfide to butyl sulfone with fuming nitric acid, results in a product difficult to purify and that the method cannot be depended upon to give constant yields

7. It was found impossible to oxidize butyl sulfide efficiently to butyl sulfone by means of nitrogen dioxide.

8. The conditions have been determined which permit the oxidation of butyl sulfide to butyl sulfone by means of sodium permanganate in yields which average 80%.

We are indebted to Miss Ethel Schram, Mr. Erle M. Billings, and Mr. Luther M. Curtice for their assistance in carrying out parts of the experimental work in this paper

ROCHESTER, N. Y.

NEW BOOKS.

Coal-Tar Dyes and Intermediates. 1st edition By E. DEBARRY BARNETT, B.Sc. Lond., A.I.C., Consulting Chemist to Bagley, Mills and Co., Ltd., formerly Research Chemist to Levinstein, Ltd., and Works Manager to the Stockton-on-Tees Chemical Works, Ltd. D. Van Nostrand Co., New York, 1919 xvi + 213 pp., 14.5 x 22.5 cm. \$3.50 net.

This is the first of a series on Industrial Chemistry edited by Samuel Rideal.

"Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture.

* * *

"An attempt will, in fact, be made to get away from the orthodox textbook manner, not only to make the treatment original, but also to appeal to the large class of readers already possessing good text-books, of which

there are quite sufficient. The book should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

* * *

"It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions "

It is quite evident from the above quotations that the series will be most useful to busy people who desire a brief description of well-known processes.

Many people will not agree with the last quotation for in America it has been found no drawback to our graduates to be unfamiliar with industrial processes. Plant research laboratories generally prefer a well trained laboratory chemist. The plant experience comes quickly when desired.

The book in question is accurate in places and gives a number of good commercial processes in a brief and readable way but it will be very misleading in a great many respects, for many of the methods are not in commercial use that are better known and are in operation. Among a few of these replaced processes may be mentioned those for amino G acid, α -naphthylamine, Laurent's acid, *m*-phenylenediamine. The method for G-acid is antiquated and American practice will not regard as commercial a process requiring a large mass to stand one week with frequent agitation as is stated in the description of crocein acid.

It is true that much work has been published on the cyanine (quinoline) dyes in 1919 after the date of the author's preface, but even so there was not much justification for the statement. "Their constitution is not known but they are probably triphenylmethane derivatives." They are methane derivatives but certainly not triphenyl.

The old sulfuric acid process described for the manufacture of phthalic anhydride is being replaced by the new method consisting of the vapor phase, catalytic, air oxidation of naphthalene.

The author's remarks in the preface regarding patents, the writing in the technical press and the research procedure from laboratory to plant are particularly pertinent.

Not much is to be expected of a book treating of commercial processes for dyes and intermediates in 207 pages, but it is unfortunate that so much readable matter is clouded with misleading information so that the ordinary reader cannot distinguish the good from the bad. H. D. GIBBS.

NEW BOOKS.

The Realities of Modern Science. By JOHN MILLS. 320 pp. The Macmillan Company. \$2.50.

Studying this book leaves the general reader, for whom it is written, with a feeling that it is "different" and worth while. It covers a certain range in physics which might be called semi-mathematical, semi-molecular. The preface seemed to promise an excessive up-to-dateness. It includes the following boldness: "The existence of electrons and their determining effect in the composition of the chemical elements are easily demonstrable facts, compared to which the indestructibility of matter is a speculative assertion and the independence of mass and speed an exploded theory."

It was a little surprising to the reviewer to have to start far back of the real realities of modern science, and among the author's fancied visions of the most ancient of prescience. Earliest man, or that ancestor who first enjoyed the warmth of an accidental fire, or dug roots for his nourishment, is given a lot of attention. This linking up of science with prehistoric time destroys much of the effect of modernness. The average Boy Scout probably already knows pretty well the useful facts represented by the first 6 chapters.

The Molecular Composition of Matter is treated in Chapter VII much as in general text-books on physical chemistry, and with Chapter VIII we arrive at the period of the electron. In this chapter we read, "An atom, we have reason to believe, always consists of a number of electrons and another part which is called the 'nucleus.' These electrons are little bits of electricity." And of the electron, in part we read, "But as to the electron itself, no explanation can be given, etc.," and, later, "But what is the nucleus? That we do not as yet know."

Of course, there is more on this subject, and better. It is unfair to give the impression that much of what is known about such things is not included in the Chapter, for it is. The ether is brought in, but no use made of it beyond such statements as that electrons must push on one another through a medium, and that a vacuum is full of ether, according to the ideas of the modern physicist. Thus for the general reader seeking the realities of modern science, the hypothetical is scrambled with the real. It seems as though the word "space" could have accomplished the desired end so far as that end is clear. I believe this chapter would have seemed less didactic and would have been more comprehensible if the author had introduced at this point some of the historical facts which led to the passage from our previous different and indivisible atoms to the universally identical negative protyle, the electron. The following can hardly seem sufficiently encouraging and helpful, and might have been made clearer by related historical facts: "For convenience and for reasons connected with the history of the science, we call the electricity of the electron negative."

If vacuum tube or arc experiments could not have been used in this chapter to give the general reader some conception of the properties of electrons, surely Dr. Millikan's wonderful and widely known oil-drop experiments could have been here introduced instead of being postponed to the back of the book.

The reviewer prefers the book which pictures briefly the facts which led scientists to accept new viewpoints, and follows such introductions with as wide general exposition of what it all means as is desirable. The trouble with the old atoms themselves was that, in the hands of some writers, they grew too hard and round, too petrified, indivisible, and impenetrable.

In an attempt to write for the general reader, the justifiable desire to be clear has called for much space. The book is full of references to things, perfectly familiar to any probable reader, which have apparently to be explained at length, and some of this matter takes the place of that which could have been used for telling about actual experimental observations of modern time. The parachute, for example, need hardly have been described, and an explanation that an automobile does not have to complete 30 miles in order to be going at a 30-mile rate is overdone, even in a laudable attempt to make calculus easy. On the other hand, as supporting certain fundamental principles, illustrations are given which lack the convincing property of obvious certainty, as, for example, the statement that substances absorb the same frequencies as they naturally emit and so heated red glass gives off a blue light. A boy who tried this might doubt the general principle.

We are told concerning matter that we must always bear in mind its granular and electrical composition, but we are scarcely shown the reasons. As they may be more real than the conclusions, the average reader will want them.

A chapter on Some Uses of Mathematics was a disappointment under this title. There are few uses in the chapter unless they are a reference to Newton's mathematical method and Maxwell's assumption that light is an electrical phenomenon. The chapter seemed to the reviewer a clear appeal for considering all phenomena mathematically or symbolically for economy's sake, and a good start to orderly conceptions.

The chapter on Rates is concerned with Galileo and with abstract definitions of rates, and not with modern science or its application, and much the same applies to the chapter on Force. Modernity is not a characteristic of them, but mathematics is.

The chapter on Molecular Motions and Temperature compares gaseous molecular motion to the flight of gnats, and draws the usual conclusions as to effect of concentration, etc. It adds very usefully the illustration of a small piece of paper tossed about by the motion of the gnats as an intro-

duction to Brownian movement. The application of the old observations of Brown (1827) has truly become a reality of modern science and one of much value. The rest of the chapter is an elementary discussion of Boyle's Law and of the derivation of thermometry. This leads to a brief consideration of the absolute zero, -273°C. , which is left to us as something "probably never to be reached experimentally." As a footnote states that helium was liquefied at -271.3° , the general reader might well ask support for the assumption that at least -1.7° may not still be subtracted in some way.

Motion of Electrons. This chapter, in the middle of the book, begins to describe some modern realities of science, if by modern we mean something developed within the past century.

On p. 204 is a cloudy statement. In reference to magnetic properties we read (after reference to iron and nickel and cobalt), "In most other substances it is practically negligible. The substances in which there is any effect whatever are called 'paramagnetic,' while those like iron are known as 'magnetic.'" One might question whether "any effect whatever" covers "practically negligible effects," and whether diamagnetic effects have disappeared?

In general there is a forced, or stilted impression created by the desire to foresee all effects on the basis of present theories. The extent to which such theories should predominate over simple and coordinated statements of observed facts is a question of judgment and a matter of opinion, but to the reviewer, it would seem more acceptable to read about the phenomena as observed and later the coördination which has become possible, for example, through the conception of electrons. One can hardly be sure what future developments may be made of electrons, but the phenomena themselves in which they seem to take part are quite regular and determinable. On the other hand, we do not like to read: "About the conductor there is said to be a magnetic field." We actually *know* there is a magnetic field there, but we may not be through our guessing as to its composition in terms of other concepts, which may have to be eternally pictured anew.

The chapter on The Continuity and Correspondence of Molecular States is clear and condensed.

"Molecular Mixtures" begins with partial gas pressures and proceeds through the usual development of osmotic pressure measurements, the rise in boiling point and reduction of freezing point, due to dissolved substances, etc. This is quite condensed and leads directly to the chapter on Electrolytic Dissociation. This subject is treated first from the modern electronic viewpoint, as though it would have been possible to guess the phenomena of conductivity of solution from electronics. Later on, the

historical development is explained as it took place, but the impression made by such arrangements, which are common in the book, is that the electron is being forced to explain "before the fact" more than is good for the understanding.

"If the reader obtains a correct concept of molecules, atoms, and electrons, many important laws will appear to him as deducible." This may all be true, but it is first through some clear, concise statements of experimental observations that correct concepts are reached. Possibly also, even then the reader will learn that some of the important laws only appear, but are not actually deducible, owing to the apparent errant nature of Nature.

In the lengthy discussion of the LeChatelier-Braun principle, some of the illustrations seem of a kind little suited to elucidating the point. The statement that a stretched wire is cooled on account of the principle, or that it resembles the organic faculty of accommodation, did not make it clearer to the reviewer, because these in themselves are no clearer. Reference to the wire experiment as a fact, would have saved the reviewer the trouble of searching for it.

Under Molecular Magnitudes, Perrin's work on colloidal particles is briefly but clearly given and is convincing. Here again Millikan's work is referred to and description seems necessary at this point. This is still postponed, however, to the back of the book. Discussion of the molecular and the mercury vacuum pump contributes to this chapter.

In the chapter on Molecular Energy there is a fine effort at coördinating the question of specific heats in general. The conception of quanta is interestingly introduced and properly left "in the hands of the future," but a more complete description of this idea might be in place in such a book.

We do not like introducing new symbols, and as most physicists are learning to use the "h" and "nu" these particular letters have probably come to stay.

The chapter on Electronic Magnitudes is by far the most interesting one. The impression gained from it is that it deals with relatively simple experiments of the utmost significance. Nothing is said about what ought to occur because of previous conceptions, but rather what did occur under the conditions of Dr. Millikan's classical experiments, those of C. T. R. Wilson (not mentioned) and Moseley. It repeatedly seemed to the reviewer that this chapter should have formed a much more prominent and an earlier part of a new book on the "Realities of Modern Science." Chapters on Machines of the Ancient World, Weights and Measures, The Beginning of Knowledge, the Beginnings of Science and the Beginnings of Experimentation, while constituting material "adapted to the future citizen

...her than the future scientist," do not contain that quality of our modern physical facts which encourages the future citizen to "carry on" until he can reach the wonderful, instructive, and interesting Realities of Modern Science

W. R. WHITNEY.

THE JOURNAL

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American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

PREPARATION OF FORMALDEHYDE.¹

BY MOYER DELWYN THOMAS.

Received December 12, 1919.

The preparation of formaldehyde was first accomplished by Hofmann² by passing air laden with methyl alcohol vapor over a heated platinum wire. The process was greatly improved later by Tollens³ and Loew,⁴ who substituted a roll of copper gauze for the platinum catalyst. In 1908 O. Blank⁵ recommended silver, precipitated on asbestos, as a much more efficient contact agent than copper. Finally Jobbling, in his monograph on catalysis, has made the statement that gold is the best catalyst of all for this purpose.

Two systematic investigations bearing on this subject have been published. Orloff⁶ studied the effect of variations in the following factors: (a) the amount of alcohol vapor in the air; (b) the speed of the gas; (c) the nature and dimensions of the catalyst; (d) the purity of the alcohol. As catalysts, copper in various forms was tried as well as platinum, mantle

¹ From a dissertation submitted to the University of Oxford, February, 1919, in partial fulfilment of the requirements for the Degree of Bachelor of Science.

² Hofmann, *Ann.*, 145, 357 (1868); *Ber.*, 2, 152 (1869); 11, 1686 (1878).

³ Tollens, *Ber.*, 15, 1629 (1882); 16, 917 (1883); 19, 2134 (1886).

⁴ Loew, *J. prakt. Chem.*, [2] 33, 324 (1886).

⁵ O. Blank, *D. R. P.*, 218697.

⁶ Orloff: "Formaldehyde," translation by Kietzbl, 1909; *Chem.*, 1908, I, 114 and 135; 1908, II, 1499.

oxides, vanadium oxide, and iron. The best results were obtained with rolls of copper gauze, when the reaction mixture contained from 0.37 to 0.6 g. of oxygen per g. of alcohol. A roll of 30 mm. diameter gave a maximum yield of 54.5% while a 15 mm. copper roll yielded 49%. The best speed of the gas past the catalyst was found to lie within the limits 140-160 liters per hour. 2% of acetone in the alcohol caused a hotter reaction and an appreciable lowering of the yield, while traces of substances containing chlorine in the alcohol poisoned the catalyst.

Le Blanc and Plachke¹ have investigated the action of a roll of silver gauze with great thoroughness. The conditions of the experiment were rigidly controlled, and it was shown that silver was a better catalyst than copper. Some of the results are plotted on the curves for comparison with the results of the present investigation. Attempts were made to measure the temperature of the catalyst, but it is evident from the work below that these attempts did not succeed.

The following investigation was undertaken at the suggestion of Professor W. H. Perkin to supply more information concerning the process of making formaldehyde. The results are particularly interesting because the corresponding yields of formaldehyde are considerably higher than the yields recorded by either Orloff or Le Blanc, though the work of these two investigators is in general confirmed.

The arrangement of the apparatus was not essentially different from that used by Tollens. Air was drawn through a loosely packed soda-lime tube into a gas meter. Then it was dried in 2 sulfuric acid bottles and led to a battery of 3 flasks immersed in a thermostat regulated to $\pm 0.05^\circ$. These flasks were joined together by well-insulated connections and both the intake and exit tubes were provided with glass taps; also each flask carried a dropping funnel. About 100 cc. of methyl alcohol was placed in each vessel and the battery was accurately weighed before and after each experiment. It was possible to secure complete saturation of the gas at all the speeds employed, with this system. The air-alcohol vapor mixture was now warmed to 100° by passing it through a coil heated with boiling water, and then led directly to the reaction chamber containing the catalyst. A hard glass tube served as a reaction chamber for the first 3 series of experiments, but it proved unsatisfactory because it could not stand the strain of the high temperatures without breaking on cooling. For the last series, an opaque silica tube was used. In all experiments the wire gauze was well wrapped in prepared asbestos in order to force all the gas to go through the roll.

The reaction chamber communicated with a large air-cooled flask in which a solution condensed containing from 33 to 50% formaldehyde and from 5 to 20% alcohol. After this flask was placed a condenser and an-

¹ Le Blanc and Plachke, *Z. Elektrochem.*, 17, 45 (1911).

other receiver; then 2 or 3 weighed wash-bottles and a sulfuric acid bottle. Only traces of alcohol and aldehyde reached the drying agent. There was now provided a gas sampling pipet containing mercury. The tap of this pipett was opened at the beginning of the experiment as soon as the air had been swept out of the apparatus, and the sample was allowed to leak in slowly throughout the entire run. Finally the apparatus led to another gas meter (provided with a manometer); then through a control tap and a large stabilizing bottle, to the pump.

At the commencement of an experiment, the catalyst was warmed to about 400° , but as soon as the stream of air was started, this external heating was discontinued. The speed of the gas could be adjusted quickly and sufficiently closely by regulating the pump and the last control tap. A run was allowed to proceed for from 15 to 90 minutes, according to the conditions. At the end the distillates and wash waters were carefully weighed and analyzed. The formaldehyde in the distillates was determined by the "sodium hydroxide-hydrogen peroxide" method¹ but the wash waters were analyzed by Romijn's iodine method.² The alcohol was found by oxidizing with chromic acid³ and making allowance for the formaldehyde present. The gas sample was analyzed in an Orsat apparatus.

It was thus possible to control each experiment in 3 different ways:

- (1) Amount of alcohol taken = alcohol accounted for in products as unchanged alcohol, formaldehyde, carbon monoxide and carbon dioxide.
- (2) Volume of nitrogen in air = volume of gaseous products less volume of carbon monoxide, carbon dioxide, hydrogen and oxygen.
- (3) Volume of hydrogen in products was compared with the theoretical amount according to the equations below. All of these comparisons showed good concordance in most of the runs.

Four series of experiments are here recorded with 4 different catalysts.

- (1) A copper spiral: Length 74 mm.; diameter 14 mm.

Weight 30.5 g.; mesh 61 (per inch).

- (2) A silver spiral: Length 75 mm.; diameter 10 mm.

Weight 13.5 g.; mesh 53.

(This gauze had been used for halogen combustions.)

- (3) A new silver spiral: Length 100 mm.; diameter 13 mm.

Weight 40.75 g.; mesh 61.

- (4) A gold-plated copper spiral: Length 100 mm.; diameter 14 mm.

Weight of copper 31.35 g.

Weight of gold 2.40 g.; mesh 35.

The effects of varying the following factors was sought: the proportion of air to alcohol vapor; the speed of gas; the length of the catalyst; and the purity of the alcohol. Curves have been drawn to illustrate the results. A serious difficulty arises when one seeks to depict graphically

¹ Haywood and Smith, *THIS JOURNAL*, 27, 1188 (1903).

² Williams, *ibid.*, 27, 596 (1903).

³ Blank and Pinkenbeiner, *Ber.*, 39, 1326 (1906).

the influence on the yield, of changing the composition of the reaction mixture, because the heating effect increases as the proportion of oxygen in the gas increases; and also as the speed is raised. Le Blanc and Plascike used constant temperature of the catalyst as the basis of this comparison, thus ignoring the effect of large differences of speed. (Also it is altogether probable that their temperatures were not constant at all.) In the curves below, constant speed of the air has been chosen for this comparison. This is equivalent to saying that the oxygen supply to the catalyst was held constant; therefore the heat of the reaction was nearly constant, though the temperature actually generated depended on the dilution with alcohol.

The alcohol used was carefully fractionated with a 5-piece Young's column. It boiled constantly at 65 ° (758 mm.), and contained 0.02% of acetone.

It was noted in the experiments with silver that the quantity of alcohol carried off at constant temperature, by the same amount of air, varied appreciably from day to day, as well as with different speeds of the air. These variations were shown by the gas law to be due to differences in the total pressure in the vaporizers. Accordingly, in the last series of experiments, a manometer was put into communication with the last vaporizing flask through the dropping funnel, and the pressure was adjusted by means of the tap on the intake tube of the first flask. Good concordance in the quantity of alcohol vaporized at constant temperature was thus obtained. It is remarkable that Le Blanc and Plascike should have had such excellent concordance in this factor without regulating the pressure.

Various attempts were made to determine the temperature of the catalyst, which ranged from a dull glow, visible only in the dark, to a bright red heat. That part of the roll nearest the entrance end of the reaction tube was always the hottest. When a thermocouple, protected by a thin-walled hard glass tube, was embedded here, it registered temperatures from 350 to 565° in both the third and fourth series of experiments. This was the range that Le Blanc and Plascike had observed also. But it seemed probable that the incoming gases exercised a cooling influence because the temperatures indicated were frequently anomalous. Therefore, when the last series was finished, a piece of gold gauze was rolled on a small, thin walled quartz tube, closed at one end, and the whole was placed in a large, silica tube, so that the open end of the smaller tube communicated with the outside. A copper-constantan couple was prepared and standardized with sulfur (444°); phosphorus pentasulfide (515°); potassium iodide (m. p. 623°); and potassium chloride (740°). This could be introduced into the center of the roll and the place of maximum temperature easily found.

The conditions which had obtained in each experiment of the series in turn were now accurately duplicated. A range from 530° to above 900° was thus found, indicating that the values previously found were quite worthless.

Experiments with Copper.

The roll of copper gauze was quite new and had the dimensions recorded above. It was well packed into a hard glass tube with Gooch asbestos. When this packing was loose the yield of formaldehyde was appreciably lower than when it was tight. The series is not complete, but enough results are given to serve as a basis for comparing copper as a catalyst with gold and silver. The optimum speed of the air was about 130 liters per hour and this speed was used throughout this series. The temperature of the catalyst was not measured. The yield of formaldehyde was calculated in 2 ways. The "process yield" is the percentage of the total alcohol taken that was converted into formaldehyde; and the "absolute yield" is the percentage of alcohol affected by the reaction which was found as formaldehyde. From a commercial point of view the second

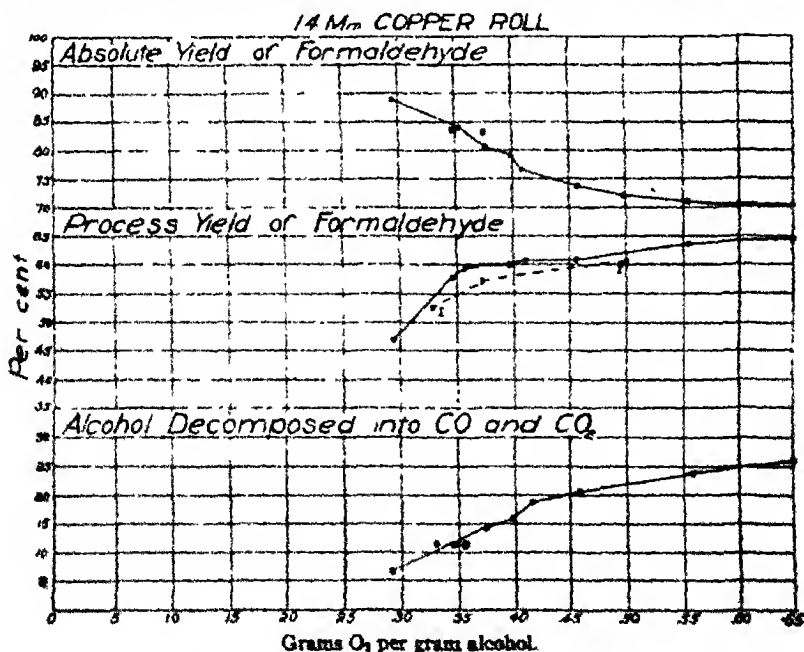


Fig. 1.

Speed of air: 115-140 liters per hour.

Curve 1.—Illustrates the influence of imperfectly packing the roll of gauze into the tube.

TABLE I.—14 MM. COPPER GAUZE.

No	Temp. of ther- mostat °C.	O ₂ per g of alcohol	Speed of air L. per hr	Alcohol accounted for in products as			Gas products						
				HCHO %	Unchanged alcohol %	CO+CO ₂ %	Total %	Yield HCHO % alcohol changed	CO ₂ %	CO %	H ₂ %	H ₂ (calc.) %	Total acc. for %
1	45.0	0.287	123	47.8	45.0	6.83	99.63	87.5	5.37
2	43.6	0.329	129	53.7	34.25	11.7	99.65	82.2	7.23	Nil	14.7	15.0	101.3*
3	42.9	0.345	140	58.2	31.2	10.75	100.17	83.3	6.27	Nil
4	42.7	0.357	126	59.6	29.45	11.0	100.05	84.5	6.53	0.22	11.9 ^b	13.2	101.5
5	41.7	0.368	114.5	59.25	27.7	11.4	98.35	83.9	6.5	Nil
6	41.5	0.375	125	57.25	27.9	11.53	98.68	81.0	7.4	0.13	13.7	13.25	100.0*
7	41.6	0.374	132	59.15	26.32	14.13	99.6	80.7	7.43	0.23	14.05	14.4	102
8	41.6	0.371	142.5	59.5	24.4	15.7	99.6	79.1	7.95	0.48	15.6	17.4	101
9	40.7	0.391	124	59.9	24.75	15.4	100.05	79.5	7.75	1.0	15.0	15.7	101.5
10	39.6	0.412	129	60.25	21.5	17.95	99.7	77.0	8.69	0.23	14.5	15.0	101.5
11	38.6	0.465	135	61.3	17.55	20.75	99.6	74.6	9.0	0.34	13.8	14.3	99.3
12	37.6	0.496	127	60.2	17.3	22.05	99.55	73.1	9.07	0.25	12.0	11.3	99.6*
13	35.7	0.562	132	63.6	12.55	24.8	100.95	72.0	8.63	0.94	8.5	8.7	101
14	31.9	0.658	128.5	63.6	9.15	26.55	99.3	70.5	7.83	1.4	Lost

* The roll was loosely packed into the tube

yield is the more important because the unchanged alcohol can be recovered by fractionation.

The curve representing the "process yield" is unique by comparison with the curves for the other catalysts, because it rises so rapidly at first as the proportion of air to alcohol is increased; then it breaks sharply and continues rising much more slowly. Also the maximum yield occurs when the oxygen content of the gas is higher than with the other metals. (See Fig. 1.) Likewise the curves representing the "absolute yields" and "total destruction" have a different form as compared with the corresponding curves for the other metals.

Experiments with Silver.

I. An old silver spiral which had been used for halogen combustions was next tried after heating it long and carefully in a flame. The first experiments gave yields that were both low and erratic. But the fifth run employed a high proportion of oxygen to alcohol and was, therefore, attended by a rather high-temperature reaction. When the preceding runs were now duplicated a regular curve was obtained. After a second strong heating, the curve was pitched still higher with respect to the yield of formaldehyde, but the series had to be discontinued because of the extremely fragile condition of the roll. This series shows clearly the harmful effects of traces of impurities, probably halogens, on the silver. But at the end of this series, the silver roll seemed to be operating in a manner almost identical with that of the new silver gauze described below, so that these impurities can be removed by heating.

II. A much more complete series of experiments than either of the preceding was now performed with a roll of new silver gauze in a hard glass tube (Table II). The reaction tube broke after the fifteenth run and the roll was damaged in shifting it to another tube. But on repeating the first experiment concordant results were obtained, showing that the damaging of the roll had a negligible effect on the process. (Table II, Nos. 11 and 12.)

It is remarkable that variations in the speed, when the composition of the reaction mixture was held constant had such a small effect on the results in spite of large temperature differences on the catalyst, which were obvious from the appearance of the metal. This series is characterized by extremely low "total destruction" of the alcohol (*i. e.*, alcohol decomposed into carbon monoxide and dioxide); combined with high "process yields" of formaldehyde (Fig. 2). The highest "process yields" were obtained when the gas mixture contained about 0.45 g. of oxygen per g. of alcohol. But the best absolute yields required less than 0.3 g. of oxygen per g. of alcohol. (Fig. 2). It was possible to obtain an absolute yield of 95.0% and a process yield of 55.5% when this ratio was 0.25 g. of oxygen per g. of alcohol.

TABLE II.—13 MM. SILVER SERIAL.

No.	Temp. of the catalyst, °C.	O. O. per % of alcohol.	Speed of air, L. per hr.	Apparent temp. of catalyst, °C.	Alcohol accounted for in products as:				Gas products.						
					HCHO, %	CH ₃ OH, %	CO + CO ₂ , %	Total, %	Yield HCHO % alcohol changed	CO, %	CO ₂ , %	H ₂ , %	H (calc.) %	Total sec. fer. %	
1	53.6	0.157	196	363	32.4	65.55	1.76	99.71	95.0	2.48	0.05	9.63	9.35	102.5	
2	50.6	0.184	180	380	40.3	57.5	2.20	100.0	94.9	2.64	Nil	12.12	12.7	101.8	
3	48.6	0.228	228	405	49.4	47.5	2.69	99.59	94.9	2.65	Nil	12.97	12.2	99.4	
4	48.6	0.218	177	400	47.1	50.0	2.82	99.92	94.5	2.78	0.05	12.42	12.8	102.0	
5	46.6	0.256	230	423	55.5	40.9	3.96	100.09	93.7	2.95	0.18	13.1	13.8	102.0	
6	46.6	0.253	196	422	55.6	41.2	3.58	100.38	93.9	3.02	Nil	13.5	13.5	102.0	
7	46.6	0.257	157	420	53.75	42.4	3.45	99.6	94.0	2.93	0.06	12.3	11.7	100.0	
8	46.6	0.253	179.4	414	52.8	43.6	3.96	100.36	93.0	3.46	0.05	12.18	12.5	101.5	
9	44.6	0.294	123	423	60.0	35.15	5.30	100.45	92.0	3.75	0.12	13.2	12.8	101.2	
10	43.6	0.325	185	444	63.7	29.4	6.57	99.67	90.5	4.23	0.20	12.3	12.9	100.5	
11	42.6	0.345	124	440	62.7	31.1	6.66	100.47	90.3	4.2	0.16	Lost	9.75	...*	
12	42.9	0.346	125	440	64.3	28.05	6.86	99.21	90.6	4.11	0.27	10.6	10.1	100.0 ^a	
13	42.6	0.354	90	403	63.2	29.0	7.77	99.97	89.0	4.88	Nil	10.6	10.55	100.7	
14	39.6	0.418	163	500	71.4	17.75	10.58	99.73	86.9	4.86	0.64	11.65	10.1	101.0 ^a	
15	39.6	0.422	121	460	72.75	16.85	10.7	100.3	87.2	5.21	0.32	11.5	11.0	100.8	
16	39.5	0.426	92	423	70.7	18.45	10.6	99.75	86.9	5.42	0.05	10.23	9.25	101.5	
17	37.4	0.480	163	565	71.35	11.33	18.3	100.98	79.5	5.65	2.55	11.3	11.35	99.7 ^d	
18	37.4	0.487	125	503	73.5	12.73	13.95	100.18	84.0	5.67	0.78	8.1	8.1	101.0	
19	37.47	0.463	95	73.1	73.1	11.32	13.8	99.25	84.2	5.54	0.99	9.9	9.75	101.0	
20	37.2	0.511	94.6	445	72.7	11.65	13.45	99.8	82.5	5.83	0.52	6.7	5.7	101.2	
21	37.45	0.479	62.5	69.9	69.9	17.4	13.65	100.95	83.75	5.9	0.43	8.8	7.1	101.5	
22	35.1	0.583	126	565	68.75	7.1	24.3	100.15	73.8	7.05	2.10	8.85	8.1	99.5	
					Length 80 mm (in two pieces)										
23	39.6	0.432	125	460	71.6	15.0	12.0	98.6	85.5	5.14	0.67	11.15	11.1	102.0 ^a	
24	39.8	0.423	128	460	71.6	18.35	9.4	99.35	88.3	4.67	0.27	11.5(?)	8.0	98.7	

^a The first expt. of this series.^b One of the final expts. Catalyst 97 mm long^c All the preceding expts. except No. 12 were done before the tube broke the first time.

It will be noted that the general form and direction of the curves are almost identical with those found by Le Blanc and Plaschke, but the yields of formaldehyde are about 10 to 15% higher and the "total destruction" about 5% lower. The reason for this variation was not determined.

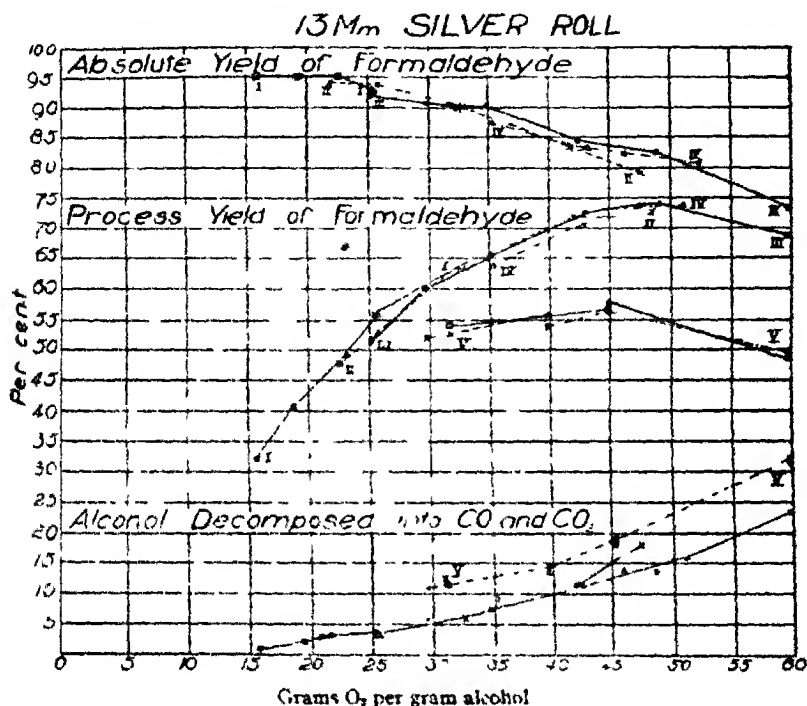


Fig. 2

Curves I—Speed of air 180-230 liters per hour.

Curves II—Speed of air 160-180 liters per hour

Curves III—Speed of air 120-130 liters per hour

Curves IV—Speed of air 90-100 liters per hour

Curves V—Characteristic results from Le Blanc and Plaschke.

Diameter of silver roll, 30 mm. Speed of air about same as indicated by notation above.

but the conditions attending the 2 sets of experiments differed in the following details. Le Blanc and Plaschke used a roll of gauze 30 mm. in diameter and worked at pressures of 770-800 mm. in the reaction chamber, whereas in this investigation the roll was 13 mm. in diameter and the pressure in the reaction chamber 715-750 mm.

Experiments with Gold.

A piece of copper gauze was electroplated with pure gold. The coating of metal was made thick and coherent by frequent scratch-brushing.

TABLE III.—GOLD PLATHED SPIRAL, LENGTH 10 CM., DIAMETER, 14 MM

No	Temp. of ther. mant. °C	Pressure in vaporizer. Cm	G O ₂ per g. of alcohol	Speed of air catalyst. L. per hr	Max. temp. of catalyst. °C	Alcohol accounted for as				Gas products				
						HCHO %	CH ₃ OH %	CO + CO ₂ %	Total %	Yield HCHO % alcohol changed	CO ₂ %	CO %	H ₂ % (calc.)	Total sec for %.
1	48.9	72.0	0.194	200	520	40.2	54.2	3.85	98.25	91.2	4.18	0.22	14.9	98
2	45.5	70.7	0.245	202	580	49.7	45.0	5.85	100.55	90.4	4.8	0.20	15.25	100.5
3	43.2	71.2	0.291	194	640	56.4	36.1	7.55	100.5	88.2	5.17	0.20	16.1	100
4	43.4	71.25	0.286	150	620	52.9	39.3	8.0	100.2	87.3	5.65	0.22	15.23	100
5	39.9	71.85	0.374	203	770	59.8	29.3	10.9	100.0	84.5	5.05	1.1	12.3	98.6
6	39.9	71.85	0.378	152	720	60.8	27.3	10.15	98.25	85.7	5.7	0.22	11.3	100.0 ^a
7	39.9	71.85	0.369	149	720	62.2	26.2	10.75	99.15	85.2	6.15	0.10	13.9	99.3 ⁴
8	39.9	71.85	0.378	100	660	54.55	32.7	13.1	100.35	80.6	7.52	Nil	13.0	97.4
9	39.9	71.65	0.377	58	585	38.3	44.6	17.7	100.6	69.0	10.15	Nil	11.4	97.0
10	37.9	71.5	0.427	195	Ca	57.5	22.7	17.8	98.0	76.3	4.7	4.25	10.8	99.2
11	37.9	71.5	0.425	152.5	850	65.0	21.1	12.65	98.75	81.6	6.25	0.40	11.7	98
12	37.9	71.5	0.422	106	735	60.6	23.65	15.2	99.45	80.0	7.58	0.22	12.9	98
13	37.9	71.5	0.422	65	605	48.5	27.6	23.3	99.4	67.3	10.9	0.05	15.75	101.7
14	35.1	72.5	0.515	156	850	63.6	18.0	17.6	99.2	78.0	5.0	2.97	6.1	99.2
15	35.15	72.5	0.516	97	790	63.0	15.0	21.4	99.5	74.4	8.4	0.55	9.95	99.3
16	32.6	72.0	0.605	150	Ca	55.0	11.3	33.0	99.3	62.5	6.35	5.3	6.95	101
17	32.6	72.0	0.608	101	850	60.2	10.3	28.1	98.6	68.2	9.2	0.70	7.45	101

18	48.9	72.0	0.194	183	520	41.4	54.6	4.35	100.35	90.6	4.45	0.30	15.6	16.9?	...
19	39.9	71.95	0.370	194	770	63.2	24.1	11.9	99.2	84.2	5.6	1.15	14.2	13.5	100
20	39.9	71.85	0.367	149	720	62.25	27.4	10.4	100.05	95.8	5.38	0.88	11.32	11.9	99.5
21	39.9	71.9	0.363	97.5	650	57.35	27.9	14.1	99.35	80.4	7.55	0.33	16.6	15.9	99.4
Length 4 cm															
22	39.9	71.85	0.368	150	720	60.0	30.2	9.7	99.9	85.9	5.35	0.60	10.1	9.75	99.5
23	39.9	71.9	0.368	106	665	59.0	29.0	12.0	100.0	83.1	6.55	0.50	12.6	12.55	99.0
Length 2 cm															
24	39.9	71.85	0.365	147	720	63.0	25.55	11.5	100.05	84.5	5.5	1.35	Lost	10.6	..
25	39.9	71.95	0.369	102	660	60.0	27.7	13.0	100.7	82.6	6.55	1.05	13.35	14.05	97.5
Influence of impurities in the Alcohol: Water and Acetone. Length of Roll 6 Cm.															
26	39.9	71.9	0.366	151.5	...	63.25	26.9	9.0	99.15	87.5	5.2	0.20	11.6	10.4	100 ^a
27	39.9	71.95	0.365	151	..	61.5	27.5	10.25	99.25	85.6	5.75	0.30	12.6	11.5	100.3 ^d
28	39.9	71.8	0.368	152	...	63.3	25.75	10.95	100.0	85.2	6.0	0.45	12.8	13.3	98.7 ^e

^a The first expt. of this series.^b The last expt. The catalyst had changed only slightly.^c 5% H₂O added.^d 10% H₂O added^e 1.7% acetone added

The experience gained in the foregoing work was used to make this series as complete and uniform as possible. An opaque silica tube was used as the reaction chamber and it withstood all the experiments without breaking. The thermostat was enlarged, to make it easier to regulate at the beginning of a run, so that it was possible to avoid a fluctuation of more than 0.05° at this time. Finally a manometer was attached to the last vaporizing flask as described above.

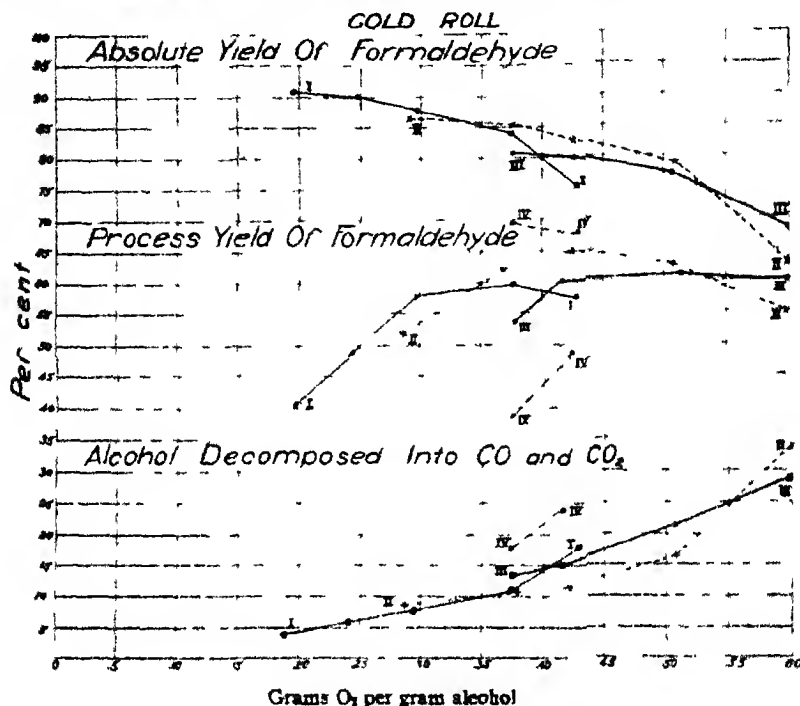


Fig. 3

Curve I—Speed of air: 200 liters per hour
 Curve II—Speed of air: 150 liters per hour
 Curve III—Speed of air: 100 liters per hour
 Curve IV—Speed of air: 60 liters per hour

Only 4 different speeds of the air were used throughout. It will be observed that speed had a tremendous influence on the process at constant composition of the gas mixture. Gold has a much greater tendency to decompose formaldehyde than silver. This also is shown by the curves illustrating the "total destruction" of alcohol (Fig. 3). With silver, speed has no influence on "total destruction;" with gold this value increases directly with the speed. When the length of the roll was cut down, the

yields of formaldehyde increased slightly and it is evident that the reaction was practically completed in the first 2 centimeters of the roll (Fig. 4). The maximum process yield (65%) was obtained when the reaction mixture contained 0.425 g. of oxygen per g. of alcohol. When this ratio was 0.245 : 1 the process yield was 49.7% and the absolute yield 90.4% (Fig. 3).

Three experiments were performed (Table III: Nos. 26, 27, 28) in which water and acetone were added to the reacting mixture by allowing the liquid to flow from a buret into the preheating coil at a controlled rate of speed. When the ratio of weight of alcohol to water was 9 to 1, the process

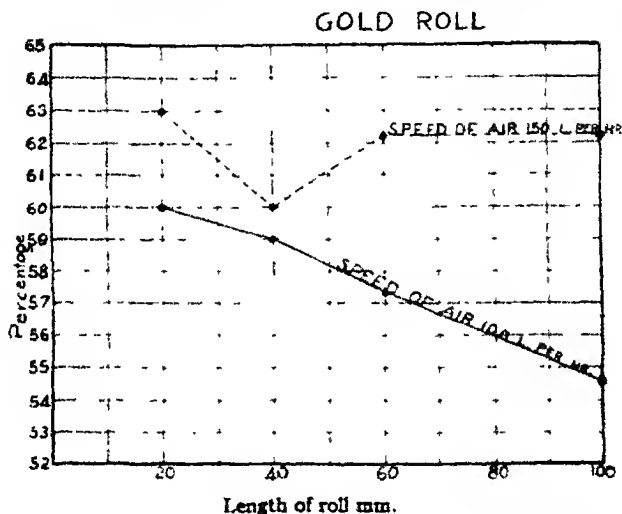


Fig. 4.

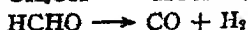
Influence of length of the roll on the "process yield" of formaldehyde.

was only slightly affected. The addition of 1.7% acetone to the alcohol caused a somewhat hotter reaction, but did not change the yield appreciably.

In Fig. 5, the total amounts of alcohol affected by the catalyst, (*i. e.*, alcohol converted into formaldehyde, carbon monoxide and dioxide), have been plotted against the composition of the reaction mixture, at constant speed of the air. One curve is given for each of the 3 metals. The values for the gold were found by interpolating from higher and lower speeds of air. Silver is thus seen to be more active than copper, which in turn is slightly more active than gold. And since silver is less active than the other 2 in decomposing formaldehyde it is undoubtedly to be preferred to copper or gold as a catalyst in this reaction

Theoretical.

The fundamental reactions of this process are no doubt the following dehydrogenations.



These are then followed by partial oxidation of the hydrogen and carbon monoxide until all the oxygen is used up.

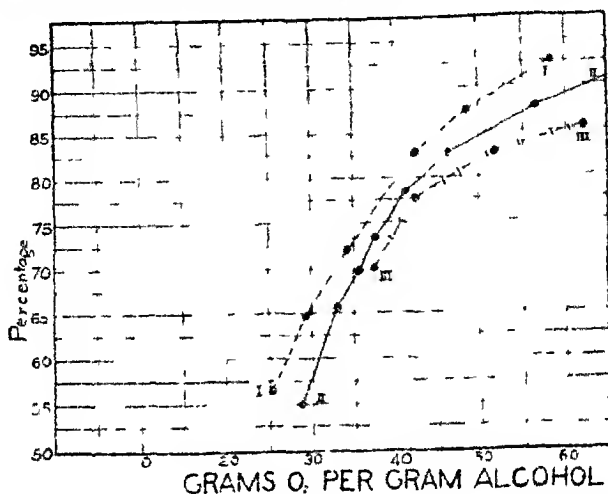


Fig 5

Alcohol converted into HCHO, CO and CO₂ by silver, copper and gold.

Curve I—13 mm silver roll

Curve II—14 mm copper roll

Curve III—14 mm gold roll

Speed of air. 125 liters per hour

The theoretical excess of hydrogen is readily calculated from these equations by means of the formula:

$$[(\text{Wt. of HCHO } 22.4/30) + 2(\text{vol. CO} + \text{CO}_2)] - [2 \text{ vol. O}_2 - \frac{1}{2} \text{ vol. CO}_2.]$$

This result is then divided by the volume of the gas products to give the percentage of hydrogen. From the tables it will be seen that this value agrees quite closely in most cases with the percentage of hydrogen actually found.

It should be noted also that Le Blanc and Plashke¹ were able to get a 27% yield of formaldehyde by passing alcohol vapor free from air over a copper spiral heated to 600 to 700°. It was observed, however, that this yield fell off gradually to 4% as the experiment was repeated, but the activity of the metal could be restored by oxidizing and reducing it.

¹ *Loc. cit.*

Accordingly the function of the oxygen seems to be, aside from maintaining the necessary temperature, to keep the catalyst active by oxidizing and removing any "poisons" and also by keeping the surface of the metal in the proper physical condition.

The amount of carbon monoxide in the gaseous products offers some interesting data for consideration. It will be seen from the experiments with gold, that the quantity of this constituent in the gas increases, (1) when the speed of the gas is increased, the composition of the reaction mixture and the dimensions of the catalysts being unchanged; (2) when the proportion of oxygen to alcohol is raised, the other 2 factors just mentioned being constant; and (3), when the length of the roll of gauze is decreased, the other conditions being unchanged. The first 2 factors involve an increase in the temperature of the reaction and in general a corresponding increase in the quantity of alcohol "completely destroyed." But in the first case the quantity of alcohol completely destroyed is usually influenced more by the length of time of contact of the gases with the catalyst than by the temperature of the reaction and, therefore, it is not so much the quantity of total decomposition that influences the carbon monoxide content of the gas. The reaction



suggests itself as a possible explanation, but this equilibrium is so slow that it could not play an important part in this phenomenon. The following table, taken from the data of the gold roll, and the work of Hahn¹ on this reaction, indicates that though the equilibrium is in every case far from complete, it is always less complete when according to the theory one would expect it to be more complete:

TABLE IV.

Grams O ₂ per gram alcohol.	Approximate maximum tem- perature catal- yst. ° C.	Length of catalyst Cm.	Liters of air per hour	CO %	$K = \frac{\text{CO H}_2\text{O}}{\text{CO}_2 \text{H}_2}$ (found)	K Calc.
0.369	720	10	149	0.10	0.02	0.64
0.367	720	6	149	0.88	0.17	0.64
0.368	720	4	150	0.60	0.105	0.64
0.365	720	2	147	1.35	0.24	0.64
0.427	950	10	195	4.25	0.69	1.4
0.425	850	10	152	0.40	0.056	1.08
0.422	735	10	106	0.22	0.025	0.69
0.422	605	10	65	0.05	0.0035	0.30
* 0.374	770	10	203	1.10	0.24	0.82
* 0.516	790	10	97	0.55	0.086	0.85

The data are insufficient to permit drawing any definite conclusion in regard to the matter, but it seems probable that the reaction is not always completed on the catalyst when the speed and the "total destruction"

¹ Hahn, *Z. phys. Chem.*, 42, 705 (1903); 44, 513 (1903); 48, 735 (1904).

are high. Under these circumstances the carbon monoxide, which is ordinarily burned completely to dioxide on the catalyst, in spite of the large excess of hydrogen, is only partially oxidized on the metal, and when the gases containing some free oxygen are swept past the catalyst the oxygen is used up by the hydrogen instead of by the carbon monoxide. No steps were taken to test this theory, however

Summary.

The results of this investigation may be summarized as follows:

1. Silver is more active as a catalyst than either gold or copper in inducing the dehydrogenation of methyl alcohol. At the same time it causes less decomposition of formaldehyde so that the yield of this product is greater with silver than with copper or gold.

2. With silver, an absolute yield of 95.0% and a process yield of 55.6% was obtained when the reaction mixture contained 0.25 g. of oxygen per g. of alcohol. Under similar conditions with gold the absolute yield was 90.5% and the process yield 50.5%. These values for copper, found by extrapolating the curves, would be about 88.5 and 40%, respectively.

3. The best process yields were obtained with silver and gold when the reaction mixture contained 0.4 to 0.5 g. of oxygen per g. of alcohol. With copper, this value was higher, 0.55-0.65 g. of oxygen per g. of alcohol.

4. The optimum speed of the air for all 3 catalysts was 125-150 liters per hour.

5. The length of the roll of gauze did not exert a very marked influence on the process.

6. The temperature of the reaction was measured for the gold roll and was found to vary from 520° to above 900° according to the conditions. The temperatures of the silver roll were probably about the same.

7. One and seven-tenths % acetone or 10% water in the alcohol did not influence process appreciably (gold roll).

8. An old silver roll which had been used for halogen combustions gave very low and erratic yields until it had been purified by several very high temperature reactions. The "poisoning" substances seem to have been retained with great tenacity.

9. Evidence is given to indicate that the essential reactions are dehydrogenations followed by the oxidation of hydrogen and carbon monoxide.

The author acknowledges his indebtedness to Professor W. H. Perkin, under whose supervision this work was carried out, for encouragement and many helpful suggestions.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

RED PHOSPHORUS AS A REDUCING AGENT.

BY LUDWIG ROSENSTEIN.

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In qualitative analysis all the group separations and by far the larger number of individual separations are based on the precipitation of relatively insoluble compounds. Such precipitation reactions are always reversible and the extent to which they proceed in the one direction or the other depends on the conditions under which the precipitation is carried out. Consequently we find many cases in which the qualitative separations by precipitation are imperfect and others in which useful results can only be obtained by strict adherence to narrowly limited conditions. On the other hand, reactions involving valence change as well as precipitation are very frequently of such a nature that broad conditions may be described under which they run to completion. For example, silver ion will react with metallic copper to give metallic silver and copper ion, and under the usual experimental conditions the precipitation of the silver is complete. Wherever such reactions can be used in qualitative analysis we may expect a sharp and unambiguous separation to a large measure independent of the experimental conditions.

With this thought in view the actions of a number of reducing agents on acid solutions of metallic salts were investigated.¹ Hydroxylamine, hydrazine, and hydrosulfurous acid were soon found to have only limited applicability; phosphorous and hypophosphorous acids gave more promising results; and it was finally found that red phosphorus, in a large number of cases, would react smoothly and completely as a reducing agent in acid solutions.

Red phosphorus as a reducing agent seems to have received little attention, although the action of yellow phosphorus and phosphine on neutral or alkaline solutions of metallic salts has been the subject of a number of investigations.² The reactions with red phosphorus, aside from their possible application to qualitative analysis, are interesting in themselves; in a number of cases metallic phosphides not previously observed are precipitated, and these phosphides, while entirely inactive toward hydrochloric acid, sulfuric acid, or alkali, are decomposed by *dilute* nitric

¹ A. A. Noyes has suggested the use of metallic silver as a reducing agent in qualitative analysis. He found that Hg, Pt, Pd, and Ru could be precipitated by shaking their acid solutions with precipitated silver. See *Z. Elektrochem.*, 9, 839-40 (1903).

² Granger, *Compt. rend.*, 127, 231 (1893); *Ann. chim. phys.*, [7] 14, 5 (1899); Cross and Higgins, *J. Chem. Soc.*, 35, 249 (1879); Rose, *Pogg. Ann.*, 6, 206 (1826); 14, 184 (1828); Rubenovitch, *Compt. rend.*, 127, 270 (1898); 128, 1398 (1899); 129, 336 (1899); Kutsch, *Ann.*, 237, 327 (1885); Oppenheim, *Ber.*, 9, 979 (1872); Sidot, *Compt. rend.*, 84, 1454 (1877).

acid, red phosphorus being one of the products of the reaction. It seemed desirable, therefore, to begin a systematic investigation of the action of red phosphorus on acid solutions of metallic salts.

This investigation is by no means complete. Some of the experiments need amplification and confirmation, and in none of the cases has the nature of the reactions received any adequate attention. Conditions are such that resumption of the work in the near future seems unlikely, so the observations, in rather fragmentary form, are presented in the hope that some one else may find them sufficiently interesting to continue.

Altogether about 120 experiments were performed; these will not be described in detail, but instead will be given a short summary of the findings under the heading of the respective ions. A large part of the experiments were performed by Mr. R. N. Donaldson in 1916, and I wish, in this place, to express my thanks to him for his faithful and painstaking work.

Of the omissions made necessary by lack of time or material, the author most regrets that experiments were not performed with ceric salts, uranyl salts, tungstates (meta and para) stable in acid solution, rhodium and ruthenium salts, thallic and thalious salts. From analogy with the cases studied it seems likely that ceric salts would be reduced to cerous; uranyl to uranol salts; meta and para tungstates probably unaffected; rhodic to rhodous salts; ruthenium salts to metal or a phosphide; and thallic to thalious salts.

Experimental Results.

The experimental results obtained will be described under 4 heads, namely: *Group A*, those ions reduced and precipitated by red phosphorus from acid or neutral solutions, Ag^+ , Cu^{++} , Hg^+ , Hg^{++} , Pd^{++} , Au^{+++} , Os^{+8} , SeO_4^{--} ; *Group B*, those ions reduced but not precipitated from acid solutions, Sn^{+4} , Fe^{+++} , Ir^{+4} , MoO_4^{--} , VO_3^- , $\text{Cr}_2\text{O}_7^{--}$, and MnO_4^- ; *Group C*, ions which were found not to react with red phosphorus in acid solutions, Bi^{+++} , Pb^{++} , Cd^{++} , Sb^{+++} , As^{+++} , AsO_4^{--} , Sn^{++} ; *Group D*, ambiguous cases, those ions with which the reduction, if any, was very slight, but for which the evidence of no reduction was not conclusive, Pt^{+4} , and TeO_4^{--} .

In all experiments, except where it is otherwise stated, red phosphorus was added in excess. Usually from 100 to 200 mg. was used.

In all these experiments both silver and copper were precipitated as phosphides and red phosphorus was oxidized to an acid lower than orthophosphoric. The pure phosphides of silver and copper were prepared by boiling red phosphorus with excess of silver nitrate and copper sulfate, respectively. The silver phosphide was grayish brown while the copper

TABLE I.

Group A. Silver and Copper Salts.—Volume 10 cc.

Salt.	Solvent.	Weight. Mg. Ag.	Time of boiling.
AgNO ₃	H ₂ O	100	5 min.
AgNO ₃	H ₂ O	10	5 min.
AgNO ₃	H ₂ O	1	5 min.
Ag ₂ SO ₄ [*]	H ₂ O	150	5 min.
Ag ₂ SO ₄ [*]	H ₂ O	1	5 min.
Ag ₂ SO ₄ [*]	6N H ₂ SO ₄	150	5 min.
Ag ₂ SO ₄ [*]	12N H ₂ SO ₄	150	5 min.
CuSO ₄	H ₂ O	500	15 min.
		Mg. Cu.	
CuSO ₄ [†]	H ₂ O	1	15 min.
CuSO ₄	3N H ₂ SO ₄	500	15 min.
CuSO ₄	6N H ₂ SO ₄	1	15 min.

Reduction complete in all experiments.

^{*} Ag₂SO₄ largely in suspension.[†] Precipitation of minute traces of copper by yellow phosphorus has been observed by W. N. Ray. *THIS JOURNAL*, 38, 887 (1916).

phosphide¹ was metallic gray With hydrochloric or sulfuric acids neither compound reacted, but *dilute* warm nitric acid decomposed them giving red phosphorus.

TABLE II.

Group A. Mercurous and Mercuric Salts

Salt.	Solvent.	Vol. Cc.	Wt. Mg	Time of boiling Mln.	Reduction	Remarks
HgCl ₂	H ₂ O	10	...	15	None	Sat. solution
	0.23 N HNO ₃	26	...	7	Complete	
	Dil. HPO ₃	25	...	5	Complete	5 drops HPO ₃ added
Hg ₂ SO ₄	6N H ₂ SO ₄	10	100	5	Complete	
	6N H ₂ SO ₄	10	10	5	Complete	
	6N H ₂ SO ₄	10	1	5	Complete	
HgNO ₂	H ₂ O	10	...	10	Complete	Sat. solution. Acid with HNO ₃ . Vigorous evolution of oxides of nitrogen.

The first 2 experiments recorded in Table II suggested that the reduction of mercuric chloride by red phosphorus is unusually slow and is apparently catalyzed by an oxidizing agent. It seemed probable that the true catalyzer was the metaphosphorous acid (HPO₃) formed by the action of nitric acid on red phosphorus, and the third experiment confirmed this supposition.

¹ Granger (*loc. cit.*) prepared a similar phosphide of copper by heating an ammoniacal solution of copper sulfate with red phosphorus.

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TABLE III.
Group A. Palladous and Auric Salts.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.
PdCl ₂	H ₂ O	10	10 Pd	5
	H ₂ O	10	1	5
	6N HCl	10	1	5
AuCl ₃	0.01 N HCl	30	1 Au	8
	3N HCl	20	1	10

Reduction was complete in all experiments.

When red phosphorus was treated with an excess of auric chloride solution a brown-black substance was formed which was unreactive towards hydrochloric and sulfuric acids, but liberated red phosphorus when treated with warm dil. nitric acid. After the action of nitric acid a reddish brown residue remained which proved to be metallic gold. The gold was, therefore, precipitated as a phosphide.

TABLE IV.
Group A. Osmic and Selenic Acids.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.	Remarks.
OsO ₄	2N H ₂ SO ₄	12	10 Os	15	Solutions were entirely free from Se.
H ₂ SeO ₄	H ₂ O	20	50 Se	25	
H ₂ SeO ₄	3N HCl	20	50 Se	5	
H ₂ SeO ₄	3N HCl	20	5 Se	5	

Reduction was complete in all experiments.

In experiments with osmiates care was taken to heat on the water bath before actually boiling to prevent the volatilization of osmic acid. This preliminary heating effected nearly complete reduction.

TABLE V.
Group B. Stannic, Ferric and Iridic Chlorides.

Salt.	Solvent.	Vol. Cc.	Wt. Mg.	Time of boiling. Min.	Reduction.
SnCl ₄	1N HCl	30	200 Sn	30	Incomplete to Sn ⁺⁺
	3N HCl	30	20	30	Incomplete to Sn ⁺⁺
FeCl ₃	1N HCl	10	500 Fe	15	Complete to Fe ⁺⁺
	3N HCl	10	10	15	Complete to Fe ⁺⁺
IrCl ₃	2N H ₂ SO ₄	30	10 Ir	21	Solution became colorless. Reduction complete to Ir ⁺⁺ . No evidence of reduction to metallic Ir or a phosphide.

The experiments with chromium compounds showed that the hexavalent chromium is reduced to trivalent and that the action was accelerated by the addition of metaphosphorous acid. In the final solution ammonium hydroxide produced almost no precipitation of chromium hydroxide in the cold. In this solution the chromium was, therefore, not present as

chromic ion. It may have been present as a chromic phosphite complex ion, as the solution contained phosphites.

TABLE VI.

Group B. Molybdate, Vanadate, Dichromate and Permanganate.

Salt.	Solvent.	Vol. Ce.	Wt Mg.	Time of boiling, Min	Reduction.	Remarks.
MoO ₃	N HCl	25	50 Mo.	5	To deep blue solution.	The reaction with KCNS is indicative of tetravalent Molybdenum
	N HCl	25		15	To light yellow solution, which gives red color with KSCN	
	4N HCl	25		2	To deep blue solution	
	4N HCl	25		7	To light yellow solution, which gives red color with KSCN	
V ₂ O ₅	3N H ₂ SO ₄	20	50 V.	8	Solution bluish green	From this solution NH ₄ OH + NH ₄ Cl produced a dirty green flocculent precipitate. The filtrate from this showed only a trace of vanadium.
	3N H ₂ SO ₄	20		25	Solution bright emerald green	
V ₂ O ₅	3N H ₂ SO ₄	20	10	25	Solution bright emerald green	
K ₂ Cr ₂ O ₇	1N H ₂ SO ₄	10	10 Cr		Slow reduction to Cr ⁺⁺⁺	
	N H ₂ SO ₄	10	10	5	Solution bright green	5 drops conc. HPO ₃ added
	2N H ₂ SO ₄	20	100 Mn	1	Immediate reduction to Mn ⁺⁺	
KMnO ₄	2N H ₂ SO ₄	20	10		Same as above	

Group C.—Solutions containing the following ions in N acid, Pb⁺⁺, Bi⁺⁺⁺, Cd⁺⁺, Sb⁺⁺⁺, As⁺⁺⁺, AsO₄⁻⁻⁻, Sn⁺⁺, were boiled with red phosphorus for 2 hours and then heated on a steam bath for 12 hours, without evidence of reaction. The experiments were tried both with and without the addition of metaphosphorous acid.

Discussion.

As no experiments with mixtures of salts were performed, it is only possible with the results in hand to suggest their application to qualitative analysis. Further work is necessary to determine the extent to which several ions present in the same solution will modify the reactions. It may be, for example, that in the presence of cupric or silver ions platonic and iridous salts will be reduced smoothly to the metals. It is very likely that the reduction of telluric and arsenic acids by red phosphorus is possible, but very slow under the experimental conditions here described,

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and that the presence of other substances may act catalytically causing reduction in these cases also.

It does appear, however, that the introduction of red phosphorus will make possible the complete elimination of the silver group, and a considerable simplification of the analysis of the aluminum and iron groups because of the reduction of the higher valence forms. The absence of cupric and mercuric sulfides from the hydrogen sulfide precipitate will also be a considerable advantage. The plan which suggests itself for beginning the analysis, assuming that the reactions proceed as indicated, is as follows:

To the solution containing the unknown substance in dil nitric or sulfuric acid add excess of red phosphorus and boil 30 min

Residue:

Ag, Cu, Hg, Au, Pd, Os, Se as metals or phosphides. Add excess of red phosphorus. Dissolve by repeated boiling with aqua regia, adding KClO_3 , if necessary. Evaporate. Take up with NHNO_3 .

Solution

Bring to proper acid concentration and pass in H_2S

Residue:

PbS , Bi_2S_3 , CdS , SnS_2 , SnS , As_2S_3 , As_2S_5 , Sb_2S_3 , sulfides of Mo, Ir, Pt and Te

Solution

Ions of the iron and aluminum groups in their lower valence forms; alkaline earths, rare earths and alkalis. Also phosphites and phosphates.

Residue:

Solution

AgCl

Cu^{++} , Hg^{++} , AuCl_4^- , Pd^{++} , Os^{+8} , SeO_4^{--}

* Osmic acid may be completely volatilized. See A. A. Noyes, *Tech. Quart.*, 16, 103 (1903).

The introduction of phosphite and phosphate into the solution is no serious disadvantage. In a large number of cases phosphates are originally present, and in any case the scheme to include phosphates is little more complicated than the scheme for solutions free from them.

Summary.

1. The reactions between red phosphorus and acid solutions of various salts have been studied and their application to qualitative analysis has been indicated.

2. The following ions in acid solution are reduced by red phosphorus as indicated: Ag^+ to insoluble phosphide; Hg^{++} to Hg ; Hg^+ to Hg ; Cu^{++} to insoluble phosphide; Pd^{++} to metal or insoluble phosphide; Os^{+8} to metal or insoluble phosphide; Au^{+++} to insoluble phosphide; Sn^{++++} to Sn^{++} , partially; Fe^{+++} to Fe^{++} ; Ir^{+++} to Ir^{++} ; SeO_4^{--} to metal or insoluble phosphide; MoO_4^{--} to tetravalent form; VO_3^- to trivalent form; $\text{Cr}_2\text{O}_7^{--}$ to trivalent form; MnO_4^- to Mn^{++} .

3. The following ions in acid solution do not react with red phosphorus: Bi^{+++} , Pb^{++} , Cd^{++} , Sb^{+++} , As^{+++} , AsO_4^{--} , Sn^{++} .

4. The following ions are reduced only very slowly or not at all: TeO_4^{--} , PtCl_6^{--} .

SAN FRANCISCO, CALIF.

CRYSTALLIZATION OF A RADIUM-BARIUM SOLUTION.

BY CLARENCE E. SCHOLL.

Received January 6, 1919.

Radium of any degree of purity may be obtained by fractional crystallization of a radium-barium solution. The crystal fractions are progressively enriched with radium while the mother liquor fractions are progressively impoverished as the number of crystallizations increases. A system containing several fractions can be divided into 2 parts: first the increasing of the radium and the decreasing of the barium content commonly called the positive series (direction) and second the increasing of the barium and the decreasing of the radium content commonly called the negative series (direction). In such a system the original material enters the system at some point between the ends while high grade radium (low grade barium) comes out the positive end and high grade barium (low grade radium) comes out the negative end. The size of the different fractions decreases gradually toward the positive end and increases toward the negative end. Any soluble impurity occurring in the system stays in the mother liquor and finally passes out of the system with the barium without causing any disturbance. Any insoluble impurity present is occluded in the crystals and is carried toward the positive end with the crystals.

The negative ion usually employed in the system is the chloride or the bromide. The bromides of radium and barium are more soluble than the chlorides. About 50% of the total chlorides crystallize out upon cooling a neutral solution from 100 to 0°, while only about 33% of the total bromides crystallize out under like conditions; yet the quantity of crystals obtained from the same volume of either a chloride or a bromide solution is approximately the same which suggests that the bromide system would be more efficient than the chloride system.

Theoretical.

The concentration of the radium in any dish in the positive direction may be calculated from the equation

$$C = AK^n,$$

where n is the number of crystallizations, A the known concentration of some dish to start with and K the factor of enrichment—the relative concentration of radium in the crystals to radium in the original material.

Thus if the concentration of radium in the original material be taken as 1.0 and the concentration of radium in the crystals is 1.6 times the

concentration of radium in the original material; the concentration of radium in the first dish becomes 1.6; the second dish, 2.56; the third dish, 4.09, etc.

The concentration of any dish in the negative direction can be calculated from the equation

$$C' = A' \left(\frac{X - K}{X - 1} \right)^m$$

where X is the inverse fractional proportion of the total weight of material occurring as crystals and m the number of crystallizations in the minus direction.

Thus with the previously mentioned conditions and half the material as crystals the concentration of radium in the first minus dish becomes 0.40, the second 0.16, the third 0.064, etc.

In any complete system of crystallizing, the positive series and the negative series must be a unified whole that is a system in which both series fit together like cog wheels. Each dish in the positive direction must conform with a dish in the negative direction. However, this does not mean that the crystals of each dish must necessarily go in the next dish positively or that the mother liquor of every dish must go in the next dish negatively. The crystals may go into the second, third, or the fourth dish positively, while the mother liquors may go into the second, third, or fourth dish negatively, depending upon the value of the enrichment factor K .

In order to find the value of K , conditions must be chosen in which A , n , m , are known. These conditions are: (1) the material used or going into the system must be uniform and of known concentration (A is constant); (2) the temperature and concentration of maximum heating must be kept uniform; (3) the temperature and concentration of minimum cooling must be kept uniform; (4) the speed of cooling must be uniform; (5) the concentration of acid must be constant; (6) the value of X must be constant; (7) the same negative ion must be used. The value of X depends partially on Conditions 2, 3, 4 and 5.

Experimental.

The Chloride System.

Hydrochloric acid in quantities ranging from 0.25 to 2.0 N was added to several portions of a radium-barium chloride solution (10^{-2} g. of radium per kg. of barium as sulfate). The dishes containing the several portions were heated on a water bath (95°) until a saturated solution was obtained—the crystals persisting 30 seconds when the solution is blown. The dishes were then removed from the steam bath, covered and allowed to cool 20 hours in a room of constant temperature at 20° . The mass was then run through a small centrifugal, the crystals weighed and the percentage

of total material calculated. The radium in the crystals and the mother liquor was then determined quantitatively according to the emanation method as developed by Wilson, Scholl, and later Lind,¹ with the following results:

TABLE I.
Radium-Barium Chloride Solutions Crystallized with Various Quantities of Hydrochloric Acid.

HCl in solution <i>N.</i>	BaCl ₂ in form of crystals. %.	Ra in form of crystals. %	Factor of enrich- ment. <i>K.</i>
0.25	44.0	72.6	1.65
0.50	50.0	81.0	1.62
0.75	51.4	82.7	1.61
1.0	54.3	85.8	1.58
2.0	58.3	87.0	1.49

When the acidity is 0.5 *N* half of the material in solution crystallizes out. This acidity was chosen for further work as it produces a value of *X* which can be expressed in a small whole integral.

Several solutions of various radium contents were taken and to each of these sufficient hydrochloric acid was added to make the solution 0.5 *N* when starting to cool. They were then crystallized as previously with the following results:

TABLE II.
Radium-Barium Chloride Solutions Crystallized with Various Quantities of Radium.

Ra in solution. G. per g. of BaSO ₄	BaCl ₂ in form of crystals. %.	Ra in form of crystals. %.	Factor of enrich- ment. <i>K.</i>
10 ⁻¹	50.5	83.0	1.64
10 ⁻²	50.2	82.0	1.63
10 ⁻³	50.0	81.1	1.62
10 ⁻⁴	50.1	80.8	1.61
10 ⁻⁵	49.8	81.0	1.63
10 ⁻⁶	49.8	80.0	1.61

Value of *K* for the chloride system under the conditions given becomes 1.62, and

$$C = A \cdot 1.6^n$$

$$C' = A \cdot 0.4^m.$$

If 1.0 be taken for the concentration of the original material then the relative concentration of the different dishes in the system will be as shown in Fig. 1. (Crystals right, liquors left.)

In this chloride system, the crystals move one dish forward for each crystallization, while the liquors move to the second dish to the left. The concentration of the later dishes is exactly the concentration of the first dishes. No other system where half the material crystallizes out can be made with any factor as the slightest variation of the factor in either direc-

¹ Bur. Mines, *Bull.* 104, 87.

TABLE IV.

Radium-Barium Bromide Solutions Crystallized with Various Quantities of Radium.

Ra in solution, G per g of BaSO ₄	BaBr ₂ in form of crystals %	Ra in form of crystals, %.	Factor of enrich- ment, K
10^{-1}	33.6	83.9	2.50
10^{-2}	33.4	82.9	2.48
10^{-4}	33.5	83.0	2.48
10^{-6}	33.3	83.1	2.49
10^{-8}	33.4	83.3	2.49

Thus K becomes 2.49 for the bromide system under these conditions and

$$C = A \cdot 2.49^n$$

$$C' = A \cdot 0.25^m$$

If 1.0 be taken for the concentration of the original material then the relative concentration of the different dishes in the system will be shown in Fig. 3. (Crystals right, liquor left.)

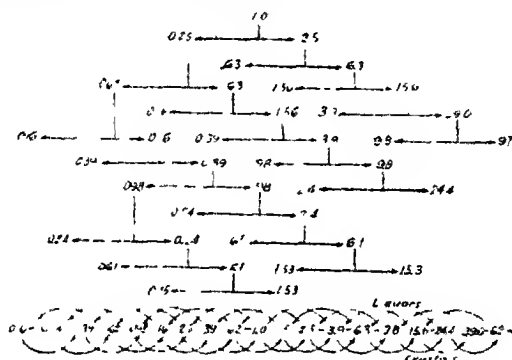


Fig. 3.

In this method the crystals move to the second dish to the right while the liquors move to the third dish to the left. The number of dishes is the same as in the chloride system for the same variation in concentration. The dishes are much smaller in size than those in the chloride system.

A simpler but less efficient method can be calculated with a factor of 2.0 and $1/4$ of the barium as crystals. See Fig. 4.

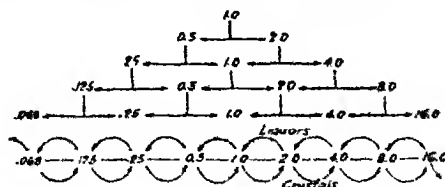


Fig. 4.

In this method the crystals move one dish to the right while the liquors move one dish to the left. This is the method¹ commonly used for crystallizing radium-barium solutions. The concentration in the negative direction actually decreases a great deal faster than is represented in the figure. Usually a great deal of unnecessary crystallization is made as the crystals always contain more radium and the liquors less radium than the system shows. The only advantage obtained is a smaller number of dishes in the system. With this exception there is no other system of any factor in which $\frac{1}{2}$ of the barium can be crystallized and still have dishes of the same concentration so that they may be combined.

There are, however, 2 variations of the system with 2.5 factor and $\frac{1}{2}$ of the material as crystals that should be considered. First, Dishes +1 and +2, +4 and +5, +7 and +8, etc., of the positive series, and -1 and -2, -4 and -5, -7 and -8, etc., of the negative series can be combined, producing a system having nearly the same concentration in the dishes as the system with a factor of 2.0, but with these differences. The liquors move 2 dishes to the left instead of one, while the crystals contain a higher concentration of radium than the next dish in the positive direction. Thus a system is obtained with less dishes in which the liquors fall in dishes of like concentration while the crystals do not. See A, Fig. 5.

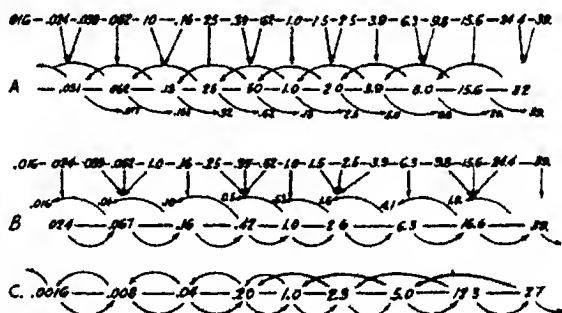


Fig. 5.—Liquors above, crystals below.

Second, Dishes +1, +2 and +3, +5, +6 and +7, and +9, +10 and +11, etc., of the positive series, and -1, -2 and -3, -5, -6 and -7, -9, -10 and -11, etc., of the negative series, can be combined, producing a system of fewer dishes in which the crystals fall in dishes of like concentration while the liquors do not. Here the crystals move one dish to the right while the concentrations of the liquors are greater than that in the second dish to the left and less than that in the first dish to the left. See B, Fig. 5.

¹ *Eur. Mines, Bull.* 104, p. 74.

These 2 variations are most suited for a practical system of crystallization. The concentrations of the dishes of the first variation correspond with the concentration of the dishes in the system of factor 2.0 and $\frac{1}{2}$ of the material as crystals, while the concentrations of the second variation are slightly higher. By placing the crystals of the first variation in the first dish to the right as in the second variation, or by placing the liquors of the second variation in the second dish to the left as in the first variation, a system is obtained in which the concentration of the different dishes would be between the concentration of the dishes in the 2 variations, with the crystals and liquors moving as in the chloride system.

Some of the efficiency of the system is lost but the number of dishes is cut in half, eliminating a great deal of labor, which more than balances the loss in efficiency.

The negative dishes can be combined further and run as stated previously, moving the crystals one dish forward and the liquors one dish backwards. See C, Fig. 5. This would put the liquor from the first dish in the enrichment series into the -1 dish. The quantity of crystals can also be increased slightly, producing a greater percentage of the radium (lower concentration) in the crystals and keeping the quantity of radium in the tailings constant and at a minimum.

Facts Noticed during Crystallization.

Some evidence was obtained that a salt of the composition of $\text{RaBr}_2 \cdot 2\text{BaBr}_2 \cdot 6\text{H}_2\text{O}$ was formed in the crystals from slightly acid solutions, having as a final product of the crystallizing system a salt containing about 39%, dry weight, of radium bromide. Higher concentrations of radium salts have been made using more concentrated acid solutions. Either on account of the small quantity of material worked with, or the effect of high concentration of radium, or the formation of this complex salt, more radium remained in solution than could be accounted for, necessitating a larger number of crystallizations.

For proportional increase in radium concentration it is more difficult to crystallize high concentrations of radium than low concentrations of radium.

The effect of a low concentration (100 micrograms of radium element per kg. of barium as sulfate) is very marked if occurring with a high concentration of acid (over 2 *N*). With these conditions the enrichment of radium is reversed, more radium (55%) occurring in the liquor than in the crystals (45%). This condition can only be remedied by evaporating to dryness and dissolving in water with the right concentration of acid.

The greater the acidity the greater the quantity of crystals and the smaller the factor. The lower the acidity in the solution the smaller the quantity of crystals and the greater the factor.

The first crystals formed in any solution contain more radium than any of the later crystals.

The concentration of radium in the crystals increases with the time of crystallization for equal quantities of crystals from solutions of the same radium concentration.

In neutral or alkaline solutions radium-barium crystals form extremely slowly upon cooling, supersaturation being noticeable. Acid in the solutions seems to act as a catalyzer in forming crystals, supersaturation being less noticeable.

Summary.

Several systems of crystallizing a radium barium solution are given with a modified form that is very efficient in crystallizing high grade radium.

The bromide system is more efficient than the chloride system

Radium is much easier to separate from barium than formerly supposed.

Several important conditions of crystallization are noted.

DENVER, COLORADO.

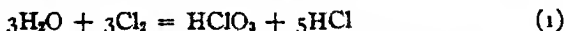
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

DETERMINATION OF THE EQUILIBRIUM BETWEEN CHLORINE, WATER, HYDROCHLORIC ACID AND CHLORIC ACID. THE FREE ENERGY OF THE CHLORATE ION.

By AXEL R. OLSON

Received January 27, 1920

The object of this research was to determine the equilibrium constant, for which no direct measurements exist, of the following reaction:



The kinetics of this reaction have been studied by various observers, in particular Sands,¹ Foerster,² Luther and MacDougall.³ Sands attempted to calculate the equilibrium constant from reaction velocities. While this method of obtaining it is correct, it involves certain differential equations which must first be determined. Luther and MacDougall have shown that the differential equation expressing the velocity of the reverse reaction of (1) is not

$$dx/dt = K(\text{ClO}_3^-) (\text{Cl}^-)^3 (\text{H}^+)^3$$

as assumed by Sands, but

$$dx/dt = K(\text{ClO}_3^-)^2 (\text{Cl}^-)^3 (\text{H}^+)^4.$$

¹ Sands, *Z. physik. Chem.*, 50, 465 (1904).

² Foerster, *J. prakt. Chem.*, 63, 141 (1901).

³ Luther and MacDougall, *Z. physik. Chem.*, 62, 199 (1908).

Moreover, Sands' calculations are evidently not accepted by Skrabal, who has made a comprehensive study of halogen reactions. He succeeded in calculating the constants¹ from kinetic measurements for the analogous bromine and iodine reactions, but has not yet succeeded in calculating the constants for chlorine. The value of the constant, as calculated by Sands, differs from this experimental determination of it by a million-fold. This enormous discrepancy is explained by the previous considerations.

The reaction expressed by Equation 1 proceeds very slowly at ordinary temperatures. Luther and MacDongall found that chlorine dioxide also was invariably formed under these conditions. To accelerate the reaction the temperature may be raised. This, however, accelerates another slow reaction also, *i. e.*, the decomposition of chloric acid into hydrochloric acid and oxygen, according to the following equation; $2 \text{HClO}_3 = 2 \text{HCl} + 3 \text{O}_2$. Since the equilibrium pressure of oxygen for this reaction is very high, a temperature must be selected which will permit the chlorine equilibrium to be attained within a reasonable time, and still not permit excessive oxygen pressure to develop. After several trials a temperature of about 90° was selected.

The method of procedure was to fill a set of glass tubes, usually 6, with a mixture of the reacting substances, seal the tubes and immerse them in a thermostat kept at 91° . Tubes were then taken out at intervals, analyzed and the concentration function calculated according to the equation

$$\frac{(\text{H}^+)^8 (\text{Cl}^-)^5 (\text{ClO}_3^-)}{(\text{Cl}_2)^3} = K'.$$

The tubes were made of Pyrex glass, and in the shape shown in Fig. 1. The function of the long, slender tip will become apparent when the analytical method is discussed. The solution for each series of tubes was made up in a flask similar to a wash-bottle. The liquid was then forced into the tubes by compressed air. In order to secure a high enough concentration of chlorine, and still keep the partial pressure of chlorine low, the solution was kept just above the temperature at which chlorine hydrate forms. Chemically pure hydrochloric acid and recrystallized potassium chlorate were used. All tubes were filled to such a height that, when they had been sealed off and heated to 91° , only a very small bubble of gas remained (approximately 0.1 cc.), and so the error made by assuming that all the chlorine was dissolved in the liquid was small. The filled tubes were then weighed, and all except one immersed in a thermostat kept at 91° . The remaining tube was analyzed in order to obtain the initial composition of the liquid for that set. The empty tube was weighed after analysis, and thus the mass of the solution in that tube determined.

¹ Skrabal, *Monatsh.*, 32, 880 (1911); 33, 116 (1912); 36, 251 (1915).

When a tube was taken out of the thermostat to be analyzed, the long tip was inserted into one of the arms of a stopcock (see Fig. 1) which had been flared out at the end so as to fit the bulging tube. The tip of the tube was of such a length and thickness that it extended into the open stopcock proper. The other arm of the stopcock was ground to fit a U-tube, B, which in turn made a ground connection with a set of Liebig bulbs, L, in which was a neutral aqueous solution of potassium iodide. DeKhotinsky cement was used to make a gas-tight joint between the tube and the stopcock at K. A slight turn of the stopcock broke the tip of the tube and permitted the liquid to run into the U-tube. When

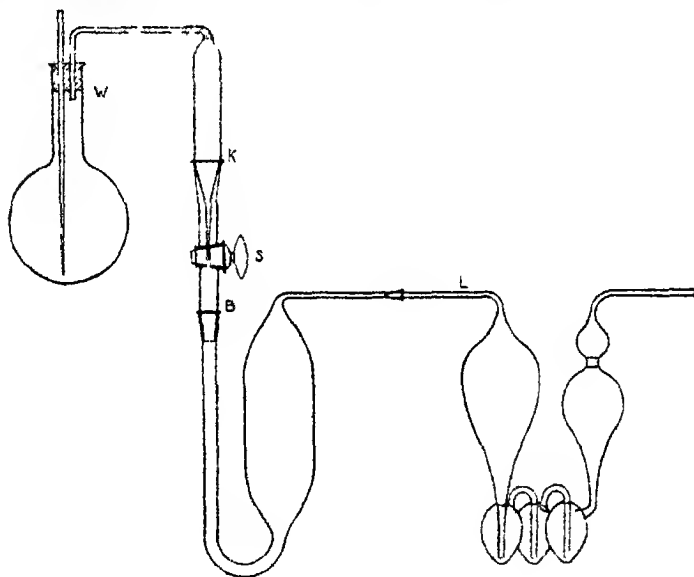


FIG. 1

the pressure had decreased a vacuum pump was attached to the open end of the Liebig bulb, the upper tip of the tube broken off, and to it a rubber tube from the wash-bottle W was attached. A slow stream of air saturated with water was drawn through the liquid in the U-tube, removing the chlorine, and then through the potassium iodide solution, where the chlorine immediately oxidized the iodide to iodine. All traces of chlorine were thus removed in a few hours. The potassium iodide showed no traces of iodine when pure air was drawn through it for a similar length of time. The iodine was then titrated with sodium thiosulfate solution. The hydrogen and chloride ions were determined by removing a sample of the liquid remaining in the U-tube with a pipet and titrating

it with sodium carbonate solution and then with silver nitrate solution, using methyl red and potassium dichromate, respectively, as indicators. Chlorate ion was determined by heating a known volume of the liquid (usually 10 cc.) from the U-tube with potassium iodide and hydrochloric acid in a sealed tube at 90° for ten minutes. Because of the small concentration of chlorate ion and the difficulty of obtaining potassium iodide, which gave a satisfactory blank test when so heated, potassium bromide was substituted for iodide in all later determinations. This gave a quantitative reduction of the chlorate and was not oxidized by perchloric acid which forms from chloric acid according to the reaction $4\text{HClO}_4 = 3\text{HClO}_4 + \text{HCl}$

The experimental data for the check on the chlorate ion determination by potassium bromide and hydrochloric acid is as follows: Several g. of potassium bromide, 10 cc. of 6 *N* hydrochloric acid, and 0.1577 g. of potassium chlorate were placed in a Pyrex glass tube. The tube was sealed and immersed in a thermostat kept at 91° for half an hour. It was then removed and cooled with tap water. The tip of the tube was broken under an aqueous solution of potassium iodide and the iodine titrated at once with sodium thiosulfate solution. It required 77.74 cc. of 0.09925 *N* sodium thiosulfate solution to reduce the iodine liberated, which corresponds to 0.1575 g. of potassium chlorate.

It has been mentioned above that Luther and MacDougall, working at 75°, found that chlorine dioxide was formed from hydrochloric and chloric acids, and, therefore, the chlorine was tested for chlorine dioxide, according to the method recommended by Bray,¹ but was found to be absent. This is doubtless due to the higher temperature and to heating in a closed tube.

Even at 90° Reaction 1 is very slow. Attempts were therefore made to find a homogeneous catalyzer for the reaction, the guiding factors being the following considerations: (1) the catalyzer must exist in at least 2 states of oxidation; (2) if *R* represents the lower state of oxidation and *O* the higher state, (a) *R* must reduce chlorate ion faster than chloride ion does, and (b) *O* must in turn be reduced by chloride ion fast enough to maintain an effective concentration of *R*; (3) neither *O* nor *R* must interfere with the scheme of analysis. $\text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++}$, for instance, would not catalyze this reaction, for in the presence of chloride the iron is almost completely in the form of ferric ion, and hence the concentration of ferrous ion which can react with the chlorate is negligibly small. A stronger oxidizing agent than ferric ion must therefore be employed, i. e., one which rapidly reduced by chloride ion at the concentrations used in this reaction.

¹ Bray, *Z. physik. Chem.*, 54, 731 (1906).

The manganous-manganic equilibrium was finally selected as fulfilling the requirements. The salt used was manganous chloride, and the concentration was about 0.02 *M*. During analysis the manganese remained as dioxide in the U-tube, and was filtered off before analyzing for chloride, chlorate and hydrogen ions. The manganese which remained in solution did not interfere with the test of the chlorate ion determination mentioned above.

The effect of the catalyzer was well demonstrated in several instances. In Series I, Tube 6 was the only one into which manganous chloride was produced; in 3 days it had progressed almost as far toward equilibrium as Tube 5, which had practically the same concentration of all the constituents, had progressed in 35 days. The tubes of Series V did not contain enough manganous chloride to produce a precipitate of dioxide. In 248 days the *K*'s corresponding to this series changed by only a factor of 10, whereas the *K*'s corresponding to the tubes in Series IV, which contained a slightly larger amount of the catalyst, changed by a factor of 4000 in 13 days.

All concentrations are expressed in mols in 1000 g. of solution. The following tables show the values found for the first series of tubes, the initial composition being chlorine and water:

TABLE I.

Series I.

No. of tube.	Vol. of tube. Cc.	Time. Days.	(Cl ₂)	(H ⁺)	(Cl ⁻)	(ClO ₃ ⁻)	<i>K</i> '
1	44.81	8	0.10076	0.0342	0.0303	0.004161	1.66×10^{-10}
2	34.79	7	0.180	0.04218	0.04437	0.002733	3.16×10^{-10}
3	53.47	14	0.1203	0.07865	0.0708	0.01198	2.90×10^{-10}
4	Broken
5	59.54	35	0.0979	0.08899	0.0707	0.013525	1.26×10^{-9}
6	53.93	3	0.09938	0.08649	0.07355	0.01379	1.26×10^{-10}

In Tube 6, as well as in all later series, a catalyzer was used.

Another set of tubes, Series II, was then filled with an analyzed solution, the concentrations of the constituents of which were such that *K*' as calculated initially from them was further away from the true equilibrium constant than that calculated from the final concentration in the last tube of the preceding set. Thus, starting with chlorine and water (Series I), *K*' initially is 0, but in the last tube in that set to be opened, No. 5, it was 1.26×10^{-9} . The tubes of Series II therefore were filled with an aqueous solution of chlorine, hydrogen chloride and potassium chlorate in such concentrations that *K*' was initially less than 1.26×10^{-9} . In a similar manner Tube No. 1 of Series III shows that the initial concentration product of that set is less than the final concentration product of the last tube of Series II.

TABLE II.

Series II.

No.	Vol. Cc.	Time Days	(Cl ₂)	(H ⁺)	(Cl ⁻)	(ClO ₃ ⁻)	K'.
1	40.19	0	0.09826	0.09028	0.10905	0.006661	5.86×10^{-11}
2	35.71	23	0.08281	0.1635	0.1569	0.009262	2.92×10^{-4}
3	34.09	209	0.06365	0.2460	0.2445	0.00822	6.16×10^{-4}
4	38.90	212	0.0788	0.2599	0.2590	0.00842	6.25×10^{-4}
5	35.01	212	0.0594	0.2435	0.2444	0.00862	7.54×10^{-4}

TABLE III.

Series III.

No.	Vol. Cc.	Time Days	(Cl ₂)	(H ⁺)	(Cl ⁻)	(ClO ₃ ⁻)	K'.
1	35.56	0	0.1049	0.1650	0.1824	0.00653	2.32×10^{-4}
2	34.10	29	0.1331	0.2317	0.2260	0.001998	7.85×10^{-4}
3	36.76	54	0.08908	0.2407	0.2320	0.006995	1.28×10^{-4}
4	33.24	69	0.08523	0.2478	0.2458	0.008579	2.87×10^{-4}
5	36.68	211	0.07025	0.2675	0.2750	0.00421	7.03×10^{-4}
6	42.71	212	0.0924	0.2881	0.2935	0.00473	7.57×10^{-4}

The equilibrium was approached from the other extreme as well. In Series IV the initial concentration of chlorine was zero, and, therefore, K' initially was infinite. When the last tube, No. 3, of this set was opened, K' had become 1.20×10^{-2} . The initial K' for the next series approaching from this side must now be larger than 1.2×10^{-2} , and the tubes of Series V fulfill this requirement.

TABLE IV.

Series IV.

No.	Vol. Cc.	Time Days	(Cl ₂)	(H ⁺)	(Cl ⁻)	(ClO ₃ ⁻)	K'.
1	57.19	1	0.06053	0.8486	0.9377	0.03452	4.22×10
2	45.20	8	0.0952	0.5825	0.6770	0.004735	3.04×10^{-1}
3	46.98	13	0.08574	0.5950	0.6601	0.001371	1.20×10^{-2}

Series V.

1	42.82	16	0.08441	0.7773	0.9973	0.0004498	1.62×10^{-1}
2	51.34	40	0.09168	0.8009	0.8426	0.0003331	6.09×10^{-2}
3	47.64	248	0.08750	0.8030	0.9125	0.0000766	1.49×10^{-2}

The tubes of Series V, because of an insufficient amount of catalyzing material, as has been explained, did not progress as far toward equilibrium as had been estimated, and so there is a slight gap in the K 's between Series V and Series VI. That the constant cannot lie within this interval is shown by the regular trend of K' in Series VI and VII.

TABLE V.

Series VI.

No.	Vol. Cc.	Time Days	(Cl ₂)	(H ⁺)	(Cl ⁻)	(ClO ₃ ⁻)	K'.
1	34.17	0	0.1089	0.5321	0.5372	0.006663	5.24×10^{-3}
2	36.70	31	0.1039	0.5120	0.5252	0.001166	7.50×10^{-4}
3	34.18	212	0.0965	0.542	0.564	0.0000766	1.23×10^{-4}
4	39.36	212	0.115	0.543	0.555	0.000086	9.18×10^{-5}
6	36.95	212	0.1054	0.540	0.574	0.0000383	5.01×10^{-5}

Series VII.

No.	Vol. Cc.	Time. Days.	(Cl ₂).	(H ⁺).	(Cl ⁻).	(ClO ₂ ⁻).	K'.
1	37.00	0	0.1102	0.3954	0.4758	0.006667	4.63×10^{-4}
2	41.33	2	0.09044	0.4086	0.4163	0.00110	8.64×10^{-4}
3	41.20	30	0.1053	0.3741	0.3807	0.0030	5.63×10^{-4}
4	36.33	55	0.09560	0.4062	0.4143	0.000833	5.22×10^{-4}
5	38.13	71	0.08863	0.4053	0.4114	0.0006663	5.0×10^{-4}
6	34.54	211	0.1210	0.4230	0.4390	0.000335	1.80×10^{-4}

The whole possible range of values of the constant from 0 to 8 was thus thoroughly covered. Since K , the true equilibrium constant, must be greater than the largest K' for the forward reaction, and less than the smallest K' for the reverse reaction, we have

$$K = \lim K'$$

$$K'_{\text{f}} - K'_{\text{r}} \doteq 0.$$

The final limiting values of the constant as determined by the converging sets differ by a factor of 2.

The results from Series II, III, V, VI and VII have been plotted in Fig. 2. Not much weight can be attached to the value of K 's in Series VI because of the exceedingly small concentration of chlorate ion. Tubes 3, 4 and 5 were analyzed the same day and yet the contents vary by a

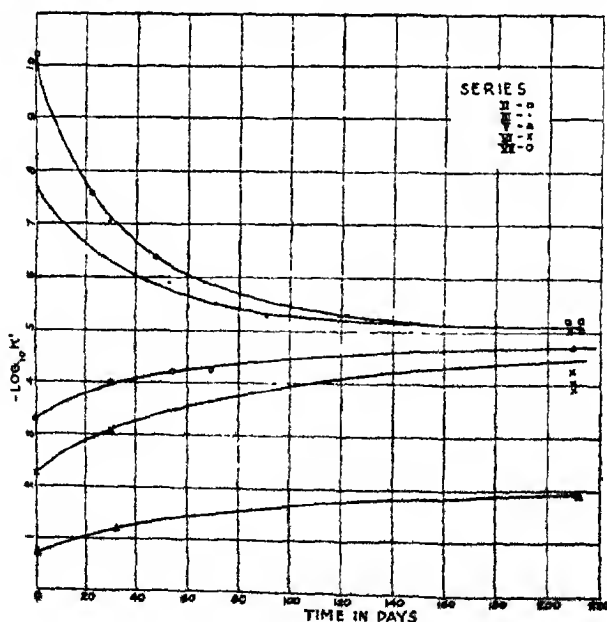


Fig. 2.

factor of 50. Series II and III approaching the equilibrium from one side are in close agreement, the final 3 measurements of the former giving an average K' of 6.65×10^{-6} , and the final 2 measurements of the latter giving an average K' of 7.30×10^{-6} . The only reliable measurement obtained by approaching the equilibrium from the other side is that of Series VII, where $K' = 18.0 \times 10^{-6}$. Thus the ratio of the values of K' from the 2 sides, which in the earlier experiments amounted to several powers of 10, has been reduced to a value between 2 and 3. Giving equal weight to Series II, III and VII, the final value becomes $K' = 10.0 = 10^{-5}$.

These values of K' have all been calculated for convenience on the assumption of complete dissociation of the 2 acids. This is justified by the fact that throughout the range of concentration of the experiments in the 3 series which have been employed the corrected degree of dissociation of hydrochloric acid is practically constant and equal to 0.77, as shown by a plot based upon the free energy measurements of Linhart¹ and of Ellis.² Assuming that the degree of dissociation of chloric acid is the same as that of hydrochloric acid, an assumption that can produce no serious error, since only one molecule of the former acid is involved, we find for the value of the true equilibrium constant

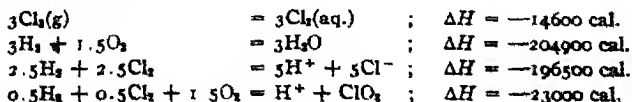
$$K = K' \times (0.77)^{12} = 4.3 \times 10^{-7} \text{ at } 364^\circ \text{ A.}$$

The free energy of the reaction can be calculated from the familiar equation, $\Delta F^\circ_{344} = -RT \ln K_{344}$, whence



In order to obtain the equilibrium constant or the free energy at the standard temperature of 250° , it would be desirable to repeat the equilibrium measurements over a wide interval of temperature. This seems hardly practicable with the catalyzer here employed. At lower temperatures the speed of the reaction would be altogether too low for the attainment of equilibrium. At higher temperatures, on the other hand, the decomposition of chloric acid to produce oxygen proceeds rapidly. For example a number of experiments were begun at 114° , but in a few weeks the pressure of oxygen had sufficed to break all the tubes employed.

It is, therefore, necessary to have recourse to thermal data. From the measurements of Berthelot and of Thomsen at about 18° the following figures are obtained:

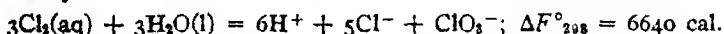


¹ Linhart, *This Journal*, 39, 2601 (1917).

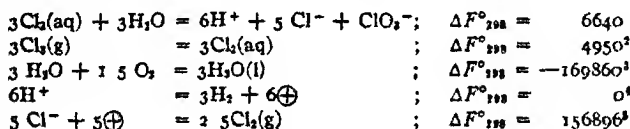
² Ellis, *ibid.*, 38, 737 (1916).

Hence, for the reaction in question, $\Delta H_{298} = 0$. This, however, will not be true at other temperatures. The partial molal heat capacity of HCl(aq) has a high negative value, namely about -40 .¹ For want of data we may assume that of $\text{HClO}_3(\text{aq})$ to be the same. The partial molal heat capacity of $\text{H}_2\text{O(l)}$ is 18, that of $\text{Cl}_2(\text{aq})$, a non-electrolyte, is doubtless small. The change of heat capacity $\Delta\Gamma$ in the reaction has, therefore, the enormous values of about -300 cal. per degree. Using the 2 equations, $\Delta H = \Delta H_0 + \Delta\Gamma T$, and $\Delta F = \Delta H_0 - \Delta\Gamma T \ln T + IT$, the value of ΔH_0 is 87300, and for the above values of $\Delta F_{0.364}$, $I = -1979.8$. This surprising value for I , which is greater than that for any other reaction studied, is doubtless due to the enormous value of $\Delta\Gamma$, which has just been mentioned above.

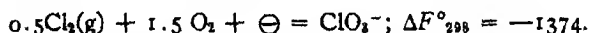
For the values of I the change of free energy in the reaction follows immediately:



In order to get the free energy of formation of the chlorate ion we must add the free energies of all the substances entering into the above reaction, thus:



From which



In conclusion, I wish to acknowledge my indebtedness and to express my thanks to Professor G. N. Lewis and Professor W. C. Bray for their help and interest throughout this whole investigation, and to Professor Merle Randall for his help in checking the free energy calculations.

BERKELEY, CAL.

¹ Lewis, *THIS JOURNAL*, 35, 1 (1913).

² Lewis and Randall, unpublished work.

³ Lewis and Randall, *THIS JOURNAL*, 36, 1969 (1914).

⁴ Lewis, *ibid*, 35, 1 (1913).

⁵ Lewis and Randall, unpublished work.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF TIN.¹ THE ELECTROLYTIC DETERMINATION OF TIN IN TIN TETRACHLORIDE.

BY GREGORY PAUL BAXTER AND HOWARD WARNER STARKWEATHER.

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A recent investigation upon the atomic weight of tin by Briscoe,² in which stannic chloride was compared with pure silver, yielded a very concordant series of results, with an average value 118.698 ($Cl = 35.457$). This value was adopted in 1916 by the International Committee on Atomic Weights in preference to the one found by Bongartz and Classen,³ 119.0, which had been in general use for some time. Very recently Brauner and Krepelka⁴ have completed the analysis of tin tetrabromide, with the result 118.699. Since the electro-deposition of cadmium and zinc in a weighed mercury cathode has been found to be a process capable of considerable accuracy,⁵ and since tin amalgam promised to be unusually well adapted for quantitative handling, the electrolytic method has been applied to the analysis of stannic chloride also. In this way it is possible, in conjunction with Briscoe's work, to obtain a complete analysis of the salt, with the use of analytical processes differing widely in character.

Purification of Materials.

Water, and hydrochloric, nitric and sulfuric acids were purified by distillation, as previously described in papers from this laboratory. Tin condensers were used with water, quartz for nitric and hydrochloric acids and glass for sulfuric acid.

Alcohol was freed as far as possible from water by distillation from lime, and was once redistilled with a glass condenser. This alcohol left no weighable residue upon evaporation.

Mercury, which had been agitated with air under conc. sulfuric acid for a considerable period and sprayed through a dil. acid solution of mercurous nitrate many times, was thrice distilled in a vacuum.

Chlorine was prepared and purified exactly as described by Baxter and Moore,⁶ by action on manganese dioxide with hydrochloric acid, and drying the gas with conc. sulfuric acid and phosphorus pentoxide,

¹ A brief account of this investigation was published in *Proc. Nat. Acad. Sci.*, 2, 718 (1916).

² *J. Chem. Soc.*, 107, 63 (1915).

³ *Ber.*, 21, 2900 (1888).

⁴ *Rozpravy České Akademie věd a umění*, 1919.

⁵ Baxter and Hartmann, *THIS JOURNAL*, 37, 113 (1913); Baxter, Grose and Hartmann, *ibid.*, 38, 857, 868 (1916).

⁶ *THIS JOURNAL*, 34, 1645 (1912); *Z. anorg. Chem.*, 80, 187 (1913).

in an all-glass apparatus. Although the generator and purifying train were thoroughly swept out with the chlorine current for some time before use, it is unlikely that the gas was wholly free from air and carbon dioxide. These impurities were less to be feared, however, than the hydrochloric acid and moisture which were removed in the purifying train.

Although the tin tetrachloride eventually was to be purified by fractional distillation, the metallic tin, from which the salt was prepared, was first freed from the greater portion of both basic and acidic impurities by electrolytically transporting the metal through an acid solution of stannous chloride. In this operation the cathode was a platinum wire, the anode a bar of block tin. The resulting bright crystals, after thorough washing, were dried and fused on an alundum boat in a current of pure dry hydrogen.¹ Before use the alundum boat had been digested for some time with constant boiling hydrochloric acid and ignited. During the fusion a white sublimate, presumably of tin chlorides, was observed. Electrodes for the production of spark spectra were now prepared by drawing some of the melted tin into hard glass capillary tubes thinly coated inside with soot, and by means of a Féry quartz spectrograph the spark spectra were photographed over the range $\lambda 2200\text{--}\lambda 5000$. The original tin contained lead and copper. Since a large part of both impurities seemed to have been removed by the electrolytic process, electrolysis was repeated in a similar fashion, using an electrolyte made from a portion of the once electrolyzed tin. Although the product still contained a very small proportion of both the copper and the lead, after being fused in hydrogen as above and cleansed with hydrochloric acid, it was used for preparing the stannic chloride without further treatment.

Preparation of Stannic Chloride.

The tin tetrachloride was prepared by the action of dry chlorine upon dry tin and was purified by fractional distillation. Two preparations were made, the methods differing only in minor details. Since the later experiment was naturally the more satisfactory, the description of the procedure will be confined to the second method.

The main portion of tin was sealed in the soft glass tube B (see Fig. 1), which was connected with the chlorine generator at A through a glass stop-cock moistened with metaphosphoric acid. The tube B was given a slight tilt toward the bulb I so that the tetrachloride would flow out of B into I as fast as formed. Bulb I contained a few grams of pure tin cast into sticks about 1 to 2 mm. in diameter by drawing the melted metal into hard glass capillary tubes. Bulb I was connected with a Sprengel pump through the side tube F, with a small bulb, *a*, and with a special valve, G.

¹ Generated electrolytically and purified and dried by passing over fused potassium hydroxide. See Baxter and Grover, *THIS JOURNAL*, 37, 1035 (1915).

The valve G, designed by Briscoe and Little,¹ deserves particular attention because it immensely facilitated the carrying out of the fractionation. The sealed-in capillary tube was closed at the end. It could be broken by the sealed glass tube filled with mercury contained in the side tube. Until it was desired to break the capillary the glass-mercury hammer rested at the end of the side tube, but by inclining the apparatus it could be made to slide down the side tube and strike the capillary with enough force to break it. To make sure of the success of the latter opera-

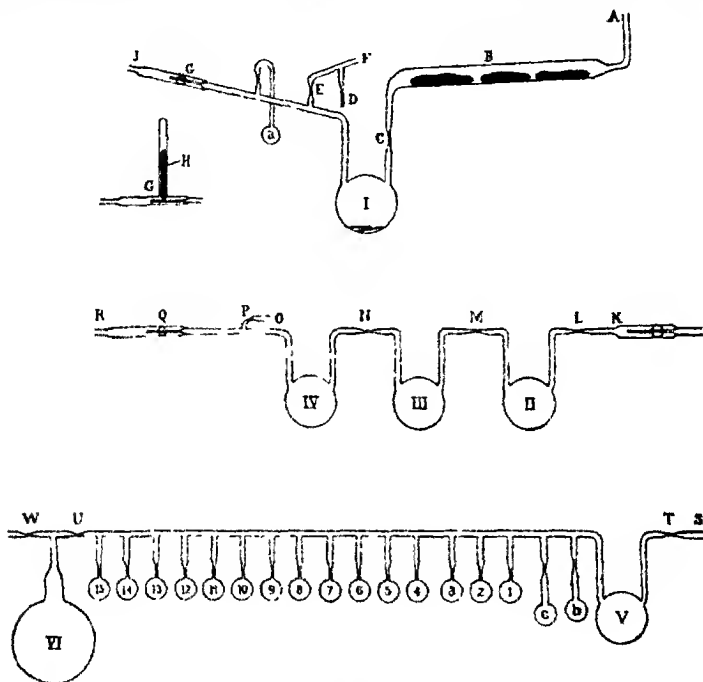


Fig. 1.

tion the capillary was scratched at several points with a file before the sealed-in joint was made. In the course of the work a joint of this sort was used 4 times, successfully in every case.

Before admitting chlorine, the bulb I was exhausted through F, D being sealed. As soon as the chlorine pressure in I became atmospheric, D was opened. The slight excess of the chlorine thus prevented air and moisture from entering the bulb I. When for any reason the current of chlorine was interrupted, D was always sealed.

The exothermic reaction between the chlorine and tin progressed so

¹ *J. Chem. Soc.*, 105, 1321 (1914).

rapidly that it was necessary to cool the tube B with a jet of air in order to prevent the melting of the tin. The liquid tetrachloride dissolved a part of the excess of chlorine and thus acquired a greenish yellow tint. After nearly all of the tin in B had been converted to chloride, the capillaries C and D were sealed, the stannic chloride in I was cooled with alcohol and solid carbon dioxide, and the bulb I was exhausted as far as possible (about 7 mm.) and maintained at this point for several hours. The residual pressure was probably due chiefly to chlorine dissolved in the liquid chloride. Then the capillary E was sealed.

The system was now allowed to stand, with occasional shaking, for about 3 weeks, in order to allow the tin to react with the excess of chlorine dissolved in the liquid, and also to reduce any lead tetrachloride which might be present. After a few days the color completely disappeared and no further change was apparent.

Next a small fraction of the tetrachloride was removed by cooling the bulb a with liquid air and when the bulb was nearly full, sealing it off at the capillary. This was done to eliminate so far as possible any hydrochloric acid which might have been formed by the action of moisture upon the tetrachloride.

The open end of the valve G was now sealed to the series of bulbs II, III and IV, which were attached at the other end to another similar valve Q, and the bulbs were exhausted as completely as possible by an efficient Topley pump through the side tube O. Finally O was closed by sealing the capillary P. During the exhaustion the bulbs and connecting tubes were heated as hot as was safe, in order to expel moisture from the interior walls of the glass. Connection was then established between the bulb I and the rest of the apparatus by breaking the capillary in the valve G. The greater part of the stannic chloride could now be distilled into bulb II by cooling the latter with alcohol and solid carbon dioxide, the temperature being maintained just above the melting point of the chloride, -33° , lest the liquid freeze and break the bulb. During the distillation the stannic chloride in bulb I was kept at room temperature by a bath of water. About 20 g. of liquid residue was left in bulb I when it was separated from the others by sealing the capillary L. Two more fractionations, from II to III and from III to IV, followed, about the same quantity of residue being rejected in each case as in the first distillation, and the bulbs II and III being successively sealed off at the capillaries M and N as soon as each distillation was over.

The connecting tubes of bulb I were frosted with a white coating insoluble in stannic chloride and in time there were deposited upon the walls of the bulb from the residual stannic chloride transparent colorless crystals. No similar deposit could be seen in bulbs III and IV, which, with I, were preserved, for several years, sealed with the residual frac-

tion of stannic chloride. We are inclined to the belief that the white coating was stannic acid formed by reaction with moisture. The colorless crystals may have been the hydrate of stannic chloride, $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$, as suggested by Briscoe,¹ who observed a similar phenomenon.

The bulb IV was next sealed through the valve Q to the train including the bulb V, the small bulbs *b* and *c* and 1 to 15, and the large bulb VI. The train was exhausted to a pressure of 0.001 mm. by means of a Töpler pump, with thorough heating to expel adsorbed gases from the glass, and was sealed at W. Next the valve Q was broken. The large bulb VI was included so as to reduce the pressure of gases other than stannic chloride vapor in the system as far as possible. After the stannic chloride had been distilled from bulb IV to bulb V the two capillaries T and U were sealed. At this point we hoped that all gaseous impurities had been eliminated, and in fact we found no evidence that this was not the case, for the bulbs of stannic chloride, when subsequently broken under hydrochloric acid, showed no sign of containing any substance but stannic chloride liquid and vapor.

In order to remove any more volatile fraction the liquid might contain, the two bulbs *b* and *c* were successively chilled with liquid air and when half full were sealed off at the capillaries. These bulbs contained, even after warming to room temperature, a small amount of colorless, crystalline solid similar to that observed in bulb I. The remainder of the liquid was collected in the bulbs 1 to 12, each bulb being sealed off at the capillary when about $\frac{2}{3}$ full. All the material in bulb 1 and the greater portion of that in 2 was condensed with liquid air. Alcohol and solid carbon dioxide were used in filling the remainder. Bulb 12 contained all of the residue which could be condensed. Bulbs 1 and 2 contained small amounts of the crystalline solid found in *b* and *c*, but none could be found in bulbs 3 to 12. Bulb V, after condensation of all the liquid possible in bulb 12 by carbon dioxide and alcohol, contained a trace of white residue, obviously deposited by the solution during evaporation.

The chief difference between the 2 series of preparations is that in the first one, owing to the fact that some of the capillary tubes connecting the bulbs in which the stannic chloride was collected were too small, diffusion was very slow and the fractionation unsatisfactory. In order to hasten the operation several of the small bulbs in which the stannic chloride was collected were chilled at the same time.

In Series I, Fractions 1 and 2 were not analyzed or otherwise examined. Fraction 15, the final residue, was converted into electrodes for spectroscopic testing. Fraction 4 was the first one analyzed, and since tin was known to have been lost during evaporation of the solution the results are not recorded. Fractions 3, 6 and 10 were lost by accidents during

¹ *Loc. cit.*, p. 71.

the analyses. In Series II, Fraction 1 was not investigated. Fraction 12, the final residue, was converted into electrodes, and Fractions 5 and 6 were lost through accidents. All other fractions of both series appear in the tables of analytical results.

In order to determine whether any metallic impurities had accompanied the stannic chloride through the fractional distillation, different specimens were dissolved in hydrochloric acid solution and the metal was deposited electrolytically as completely as possible with platinum wire electrodes. The amalgams of analyses 13, 14 and 15 were combined and made the anode under dil. hydrochloric acid, the metallic tin being deposited upon a platinum wire cathode.

The specimens examined and the impurities found are as follows:

Series I	II (residue)	Pb, Cu
	15	Pb, Cu
Series II	III (residue)	Pb, Cu
	b, c,	Pb, Cu
	3, 4, 11	None
	12 (residue)	None

The proportions of lead and copper found were extremely minute. By comparison with spectra of alloys containing known proportions of these elements, we estimate the proportion of each impurity to be less than 0.001%. While the fact that lead seems to accompany the stannic chloride during the distillation was unexpected, although lead tetrachloride is a volatile liquid, the persistence of the copper is even more remarkable. At all events the proportion of neither is enough to affect the result by an important amount.

Method of Analysis.

After being weighed, the bulbs of stannic chloride were broken under dil. hydrochloric acid and the glass was collected and weighed. Then the solution was electrolyzed in a weighed glass cell in which was sealed a platinum cathode and anode, the cathode being covered with a considerable quantity of mercury. The electrolytic cells resembled those used by Baxter and Hartmann, and Baxter, Grose and Hartmann,¹ but for reasons to be explained later had a far larger capacity for the electrolyte.

The bulb containing the stannic chloride was thoroughly cleansed outside with cleaning solution, washed, wiped with a clean cloth and dried in a vacuum desiccator over fused sodium hydroxide for at least 24 hours. Then it was weighed in air by substituting weights for the bulb, the temperature and humidity in the balance case and the atmospheric pressure being noted. The weight of the bulb under water was next found, and

¹ *Loc. cit.*

the volume calculated from the loss in weight and the temperature of the water. The vacuum correction of the bulb could now be computed from the volume, pressure, temperature and humidity of the air displaced.

In a preliminary experiment the bulb was broken under 0.3 *N* hydrochloric acid, the glass was collected on a filter and the filtrate and washings were evaporated to about 30 cc. before electrolysis.

In this experiment the quantity of tin obtained was considerably less than was expected. As a loss of tin tetrachloride during the evaporation was feared, this point was tested by distilling a solution of 10 g. of stannic chloride in 250 cc. of 0.3 *N* hydrochloric acid and testing the distillate for tin with hydrogen sulfide. No tin was found until more than $\frac{1}{2}$ of the liquid had been distilled. In a repetition of the experiment with a solution of 10 g. of stannic chloride in 100 cc. of 6 *N* hydrochloric acid tin was found in increasing amounts in the successive portions of distillate.

On the whole, the safest method of avoiding the difficulty seemed to be to electrolyze the solution of stannic chloride directly without evaporation. Electrolytic cells with a capacity for about 125 cc. of electrolyte were, therefore, constructed. The weighed bulb containing the stannic chloride was broken under 70-100 cc. of 0.3 *N* hydrochloric acid in a large, thick-walled test-tube. Although much heat was evolved, the reaction was not violent enough to cause loss by spattering, and no bubbles of gas ever reached the surface of the liquid. After being stirred the solution was filtered through a filter paper in a quartz funnel into the cell, which had been weighed with a charge of mercury. The glass and test-tube were rinsed with cold 0.3 *N* hydrochloric acid into the cell until it was nearly full and then into a large quartz dish. In all about 800 cc. of acid was used in washing the glass. The filter with the glass was ignited gently in a platinum crucible and the residue was weighed. The glass, after ignition, showed no evidence of containing tin. The ash of the filter was only 0.11 mg.

In order to show that this method of determining the weight of the glass involved no gain or loss, in several experiments an unsealed bulb similar to those used in collecting the stannic chloride, after being weighed in a platinum crucible, was broken under an acid solution of stannic chloride, and the fragments were washed and collected upon a filter in exactly the same way as in an analysis. The filter was burned in the same crucible, and the change in weight, corrected for the ash of the filter, determined. As the following table shows, a very slight average loss is indicated, owing probably to solution of the glass in the acid. This loss is so small in comparison with the weights of material used, that no attempt has been made to apply a correction.

Excess in weight of crucible + bulb over counterpoise. G.	Excess in weight of crucible + glass over counterpoise. G.	Loss. G.
2.74104	2.74097	0.00007
2.78502	2.78494	0.00008
2.69270	2.69267	0.00003
2.75258	2.75257	0.00001
2.59472	2.59462	0.00010

Average, 0.00006

The dilute washings in the quartz dish were evaporated with a small amount of sulfuric and about 10 cc. of conc. nitric acid, over an electric stove. In this way the hydrochloric acid was oxidized before the solution became sufficiently concentrated to introduce danger of losing stannic chloride by volatilization.

Before commencing the electrolysis the column of bulbs ground into the neck of the cell to catch spray was rinsed with constant boiling hydrochloric acid in order to prevent hydrolysis of any tin salt which might be projected into the bulbs. A current of 1 to 2 amperes was then passed through the cell, immersed in pure water, until chlorine ceased to be evolved. Usually this required 18 to 24 hours. At this point nearly all the tin had been deposited in the mercury cathode, but a considerable residual conductivity of the electrolyte was due to perchloric acid formed during the electrolysis. The column of bulbs was now rinsed into the cell and the aqueous contents of the cell were removed and placed in the quartz dish containing the evaporated rinsings of the glass of the bulb. The amalgam was rinsed a few times with water and the washings added to the contents of the dish. Then the solution in the dish was evaporated over an electric stove until all volatile material except the sulfuric acid and stannic sulfate had been expelled. This residue was dissolved in water, the solution was returned to the cell and electrolysis was continued for several hours.

Next the electrolyte was siphoned from a point near the surface of the mercury while the purest water saturated with electrolytic hydrogen was added at the top of the cell with the full potential of the battery, 16 volts, applied at the electrodes, care being taken not to break the electrical circuit. As soon as the reading of the ammeter in the circuit became zero, all the remaining aqueous liquid was removed and the amalgam was further rinsed, first with water, finally twice with alcohol. During the washing the cell was inclined and slowly rotated, so that liquid trapped between amalgam and cell wall might be removed. In order to prepare the cell for weighing, the outside was rinsed with water and wiped with a clean, lintless cloth. The special stopper was inserted and the cell was placed in a tubular vacuum desiccator containing fused sodium hydroxide, which was exhausted by means of a Geryk pump. Care was taken to reduce the pressure slowly at the end so as to avoid spurting of the amal-

gam. As soon as evaporation of the alcohol was complete, the cell was transferred to a second vacuum desiccator, which was immediately exhausted. After several hours the cell was weighed by substitution for a similar counterpoise containing mercury, which also was kept in an exhausted desiccator between weighings.

In order that the cell and mercury might be subjected to the same influences before and after use in an analysis, it originally was partly filled with dil. sulfuric acid, which was electrolyzed for from 2 to 12 hours with 1 ampere. It was then treated as described above, previous to the initial weighing.

The combined electrolyte and washings were evaporated nearly to dryness in a quartz dish over an electric stove, and transferred to a weighed platinum crucible. A small amount of nitric acid was added to insure complete oxidation of the tin to the stannic condition, and the solution was again evaporated, first on the electric stove, then over a flame, until the crucible was barely red for an instant.

In computing the correction for this residue the assumption is made that the tin was all in the form of stannic sulfate. But although tin was actually found to be present, it is probable that part of the residue consisted of sulfates of alkalis extracted from the glass of the cell. However, since the percentage of tin in stannic sulfate and the percentages of sodium and calcium oxides in the sulfates are not very different, 38, 43 and 41, respectively, and since the weight of the residue usually did not exceed 3 mg. and in only one case exceeded 4 mg., the uncertainty from this source cannot be large.

When the cell and the residue had both been weighed, the residue was dissolved in very dil. sulfuric acid¹ and returned to the cell, where it was electrolyzed for several hours, frequently overnight. The cell and electrolyte were then treated as before, and if a change in the total weight of tin was observed the process was repeated until the total remained constant within 0.1 mg. Occasionally only 2 electrolyses were necessary, but frequently a perceptible diminution in weight was observed in the second electrolysis. In this case usually the second and third weights agreed.

We are inclined to impute the slight loss to liquid trapped either under or in the amalgam. The fact that considerable solid amalgam always was present may account for this. In order to eliminate this error so far as possible, in the later analyses, where the quantity of stannic chloride was larger and the danger greater, the amalgam was liquefied by raising the temperature with a heavier current, and then cooling the cell before drawing off the electrolyte.

In the second series of fractions some of the bulbs were so large that it

¹ This process was omitted in Analyses 1, 3 and 5.

was necessary, on account of the violence of the reaction, to increase the volume of acid under which the bulb was broken. Here the original liquid, about 125 cc., was immediately electrolyzed in the cell. The residual electrolyte was taken out and preserved, and the first 125 cc. of washings was electrolyzed. Then the first and second electrolytes, together with the dilute washings, were combined, evaporated and treated as before.

In several analyses a slight black deposit was formed on the inner wall of the glass cell, insoluble in acid but soluble in chlorine. It was suspected that the deposit was platinum, dissolved from the anode by the chlorine evolved during electrolysis, but reduced by the stannous chloride. In one case the deposit was dissolved in aqua regia, great care being taken not to allow the solvent to touch either anode or cathode. When the solution had been evaporated to small bulk, a drop of cesium chloride gave an immediate yellow precipitate. It is obvious that the formation of this deposit involves no gain or loss in weight of the cell.

In Analyses 1 to 10, about 150 g. of mercury was used in each experiment; in Analyses 12, 13 and 15, about 200 g., and in Analyses 11, 14 and 16, 250 g.

Because of the large weight of the loaded cell, it could not safely be weighed on the No. 10 Troemmer balance used in weighing the bulbs and crucibles. Instead, in Analyses 1 to 5, a large Sartorius balance, sensitive to 0.2 mg., was employed; for all others a No. 6 Troemmer was secured, sensitive to 0.05 mg. with a load of 500 g. Weights were standardized by the Richards method of substitution. The cells and crucibles were weighed by substitution for counterpoises of very nearly the same shape, size and volume.

The amalgams were uniformly bright and lustrous. In order to show that oxidation is negligible, a bright lump of tin which had been fused in hydrogen on an alundum boat was dropped into a cell containing mercury and was weighed at intervals.

	G.
Weight of cell + amalgam (initial)	C + 6.34944
Weight of cell + amalgam after 2 days	C + 6.34943
Weight of cell + amalgam after 3 days	C + 6.34942

Further evidence on this point, as well as on the accuracy of the electrolytic process in general, was obtained as follows: A button of tin which had been fused in hydrogen on an alundum boat was placed in a platinum gauze basket and supported upon the anode of a cell which had been prepared for weighing. After the system had been weighed, 2*N* hydrochloric acid was added, the tin was electrolytically transported from anode to cathode, and the hydrochloric acid decomposed by electrolysis. The amalgam was washed and dried, and the electrolyte was evaporated, a

previously described. When the amalgam and residue had been weighed, the residue was dissolved in acid, returned to the cell and electrolysis repeated.

		I. G.	II. G.
Weight of tin		1.98341	7.19
Weight of cell		4.01336	
Weight of cell + tin		5.99677	9.43879
Weight of cell + amalgam	1	5.99654	9.43859
Weight of residue	1	0.00057	0.00039
Corrected weight of cell + amalgam	1	5.99676	9.43873
Change in weight	1	-0.00001	-0.00006
Weight of cell + amalgam	2	5.99653	9.43843
Weight of residue	2	0.00069	0.00075
Corrected weight of cell + amalgam	2	5.99679	9.43872
Change in weight	2	+0.00002	-0.00007

The close agreement of the weight of the factors with that of the products is a sufficiently rigid test of this method of determining tin. Furthermore, some time after the last 2 experiments had been completed, Mr. C. H. Wilson obtained additional evidence that the weight of the tin and mercury together is equal to the weight of the amalgam corrected for the weight of the residue, although in the case of zinc and cadmium a very slight excess in the weight of the products seems to be characteristic. This point will be considered in detail in a later paper.

In computing the vacuum corrections for tin amalgam, account was taken of the fact that a saturated solution of tin in mercury contains only 0.97% of tin at 15° and 1.21% at 25°, so that a large proportion of the tin obtained in the analyses was weighed in the form of solid amalgam. By extrapolating the results of Richards and Wilson¹ the density of a 1% liquid amalgam seems to lie between 13.460 and 13.475 at 20°. Using the average value, 13.468, the vacuum correction for 1 g. of tin dissolved in mercury to form a 1% amalgam is -0.006 mg. On the other hand, the correction for tin in the form of solid amalgam is somewhat larger and positive in sign.

Substance.	Temp. °C.	Density.	Vacuum correc- tion for 1 g. Sn. Mg.
Hg ₂ Sn	11.3	11.456 ^a	+0.016
Hg Sn	14.2	10.369 ^a	+0.017
Hg ₂ Sn	26	11.382 ^b	+0.018
Hg Sn	26	10.345 ^b	+0.018

Average, +0.017

^a Matthiessen, *Pogg. Ann.*, 110, 21 (1860).

^b Kupfer, *ibid.*, 112, 445 (1861).

¹ *Carnegie Inst. Pub.*, No. 118 (1909).

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From the quantity of mercury used in each experiment and the weight of tin obtained, the vacuum corrections for the tin in the form of liquid and solid amalgams were computed in each case.

THE ATOMIC WEIGHT OF TIN.

Cl = 35.457.

Series I.

No of analysis.	Fraction	Weight of SnCl ₄ in vacuum. G	Weight of tin in amalgam in vacuum G	Weight of residue G	Total weight of tin in vacuum G	Sn 4Cl	Atomic weight of tin
1.....	7	13 5943	6.1927	0 0021	6 1935	0 83687	118 691
2.....	13	10 7469	4 8956	0 0024	4 8965	0 83695	118 703
3.....	11	12 2869	5 5959	0 0062	5 5983	0 83699	118.709
4.....	8	10 0897	4 5962	0 0022	4 5971	0 83696	118 705
5.....	9	11 4319	5 2069	0 0028	5 2080	0 83677	118 678
6.....	12	12 20889	5 56205	0 00212	5 56286	0 837020	118 713
7.....	14	11 54233	5 25760	0 00226	5 25846	0 836818	118 684
8.....	5	11 64269	5 30452	0 00120	5 30498	0 837050	118 717

Series II.

9....	7	15 04889	6 85605	0 00235	6 85695	0 837037	118 715
10...	8	18 36074	8 36361	0 00381	8 36507	0 836869	118 692
11....	9	21 58929	9 83561	0 00302	9 83676	0 836991	118 709
12....	10	17 22210	7 84665	0 00138	7 84718	0 837040	118 716
13....	4	17 29151	7 87737	0 00297	7 87850	0 836980	118 707
14....	3	16 23310	7 39587	0 00202	7 39664	0 837059	118 718
15....	11	15 70516	7 15512	0 00201	7 15589	0 837018	118 713
16....	2	15 65437	7 13141	0 00148	7 13198	0 836852	118 689

Total..	..	230 6487			105 0893	0 836969	118 706
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Average of Series I.	..				0 836929	118 700
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Average of Series II	..				0 836955	118 707
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Average of Series I and II	...					118 703
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In Analysis 8 amalgam was lost through spattering after the first weight had been obtained. This weight is somewhat uncertain, since the appearance of the amalgam was not as lustrous as usual. In Analysis 10 a similar loss of mercury was suspected in the third electrolysis, so that although the result of the second electrolysis was considerably less than that of the first, the second weight is the one recorded. In Analysis 11 five electrolyses in all were completed, the extreme weights differing by 0.45 mg., the last 3 by 0.19 mg. The fourth weight, which was the lowest, is given in the table.

If the results for the atomic weight of tin are arranged in the order in which the fractions were distilled, only irregular variations are apparent. Hence there can be little question that the different portions were essentially identical in composition.

The final average, Sn = 118.703 (Cl = 35.457) is in very close agreement with the one obtained by Briscoe by comparing tin tetrachloride

with silver, 118.698. The percentage of tin in stannic chloride found by us is 45.562, while Briscoe found 54.439% of chlorine. The sum is 100.001%, a highly satisfactory and convincing outcome. The more recent experiments of Brauner and Krepelka also are in entire accord with the above result.

It is a great pleasure to express our gratitude to the Carnegie Institution of Washington and to the Elizabeth Thompson Science Fund for very generous assistance in providing indispensable apparatus.

CAMBRIDGE, MASS

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF BOHEMIAN CHARLES UNIVERSITY OF PRAGUE.]

A REVISION OF THE ATOMIC WEIGHT OF TIN.¹ I.

BY BOHUSLAV BRAUNER AND HENRY KREPELKA

Received February 13, 1920

In his critical discussion on atomic weight determinations,² Brauner has given the following summary of all the earlier atomic weight determinations of tin.

	Ratio	At wt
Gay-Lussac 1811	Sn SnO ₂	117.65
Berzelius 1812	Sn SnO ₂	117.65-118.08
Mulder 1849	Sn SnO ₂	117.00-116.30
Vlaanderen 1858	Sn SnO ₂	118.16
Dumas 1859	a Sn SnO ₂	118.06
	b SnCl ₄ 4 Ag	117.98
V d Plaats 1885	a Sn SnO ₂ (oxidation)	118.09
	b SnO ₂ Sn (reduction)	118.07
	a Sn SnO ₂	119.34
Bongartz and Classen 1888	b (NH ₄) ₂ SnCl ₆ Sn	119.09*
	c K ₂ SnCl ₆ Sn	119.07*
	d SnBr ₄ Sn	118.97*
	e Sn(SnS ₂) BaSO ₄	119.05*
The Mean of starred values		119.05

While our work was being carried on, Briscoe³ and Baxter and Starkweather⁴ published the values 118.69 (SnCl₄:4Ag) and 118.703 (Sn:4Cl), respectively. On account of the embargo placed by Austria on English publications during the war the present authors were entirely ignorant of both above-mentioned researches until some time after the armistice was signed.

Until the year 1888 the atomic weight of tin had been taken as 118;

¹ Presented to the Bohemian Academy of Sciences, Prague, 1917.

² Abegg's "Handbuch der anorg. Chemie," Group 4, 529.

³ *J. Chem. Soc.*, 107, 76 (1915).

⁴ *Proc. Nat. Acad. Sci.*, 2, 718 (1916).

later as 119. Brauner points out that the earlier value (118) is necessarily too low, as in converting tin into the dioxide the weight of the latter is increased by the weight of occluded products of decomposition of nitric acid. On the other hand, Brauner regards the value, 119, as too high, since Bongartz and Classen worked with or finally used electrolyt tin; obtained in this way, tin cannot be entirely pure (*i. e.*, 100%) and its occluded impurities would cause a proportionate increase in atomic weight. The error in the accepted atomic weight was 0.35, indicating that tin such as they used contains approximately 0.3% of occluded matter. The same opinion is held by Cohen, the prominent Dutch expert on tin.

The work described in this paper, stimulated by the above considerations, included an examination of the respective worths of methods hitherto used in determining the atomic weight of tin, an examination of the purity of electrolytic tin, and finally a revision of the atomic weight, correcting the high value in the International Table.

A. Oxidation of Tin by Nitric Acid.

The material with which we started was tin foil, containing, according to Mylius' analysis, only 0.004% of foreign matter. This tin foil was oxidized by dil. nitric acid in a platinum crucible. The metastannic acid thus formed was heated in an electric furnace to 900°, but it was found not to give constant weight even after 3 or 4 heatings. Possibly the adsorption of air on the large surface of stannic oxide increased the total weight.

0.2239 g. of stannic oxide differed in single weighings by from 0.00005 to 0.00015 g. The orientation values obtained in this way did not differ much from older determinations,¹ although the metallic material we used was far purer than that used by the earlier investigators. The mean of 3 determinations gave 118.02 for the atomic weight.

B. Removal of Occluded Products.

In order to set free the occluded gaseous products of nitric acid and to prevent adsorption we heated stannic oxide obtained on oxidation, with remelted potassium sulfate. Thus 3 syntheses were made, whose mean gave, as expected, a higher value, 118.66.

	SnO ₂ given by 1 g. of Sn	At. wt.
Mean of results A	1.27121	118.02
Mean of results B	1.26960	118.66
Difference.	-0.00161	+ 0.64

This difference denotes mainly the quantity of adsorbed air and liberated gaseous products which had been occluded.

¹ Berzelius, 118.08; Dumas, 118.06.

C. Electrolysis of Diammonium Stannic Chloride.

For the preparation of pure substance Classen's methods¹ were used. The electrolytic process, however, was modified: the cathodes used consisted of tin only, prepared from pure tin. By this arrangement the over-voltage of hydrogen evolution was considerably increased (amounting to 0.5 volt for normal solutions of tin, according to Caspari); moreover, use of tin cathodes made it possible to remelt the electrolytically deposited tin, together with the cathode. A weighed quantity of ammonium chlorostannate $((\text{NH}_4)_2\text{SnCl}_6)$ was dissolved in a solution of ammonium hydrogen oxalate, saturated in the cold. The electrolyte was kept above 20° , the transition point of gray tin. The compact tin-coating, consisting of well-defined silvery crystals, was weighed, together with the cathode after a thorough washing in water and drying at 120° , and placed in a porcelain boat, the cathodes having the form of the boat, and remelted in a current of hydrogen. Subsequently it was oxidized at a temperature above the melting point of tin and again reduced by hydrogen.

Hydrogen, evolved in Kipp's apparatus by means of redistilled sulfuric acid acting on pure zinc free from arsenic, was passed through a system of washing flasks, containing 20% sodium hydroxide solution, 15% silver nitrate solution and distilled water, then over red-hot copper-wire gauze, and into the reducing tube of combustion glass, at the end of which the gas was ignited. Single connections in the system were made by means of ground glass joints. Oxygen from a gasholder was washed with water and led into the oxidizing tube. Thus the following 5 electrolyses were made:

TABLE I.—TIN FROM THE ELECTROLYSIS OF DIAMMONIUM STANNIC CHLORIDE.

$(\text{NH}_4)_2\text{SnCl}_6$ G	Density of current		Sn before melting G	Sn after melting G	Δ	Sn
0 66721	0 1 A	0 2-0 5	0 21589	0 21598	+0 00009	119.11
0 94915	0 2A	0 6A	0 30723	0 30717	-0 00006	119 06
1 19720	0 1A	0 5A	0 38753	0 38732	-0 00021	119.00
1 93170	0 15A	0 45A	0 62475	0 62456	-0 00019	118.89
4 21585	0 2A	0 3-0 5A	1 36463	1 36451	-0 00012	119.08

Mean = 119.03

In all these cases a compact coating of silvery tin crystals was deposited. After the first remelting in hydrogen a silvery grain was obtained, on the surface of which carbon was distinctly visible, identified afterwards by dissolving the tin in hydrochloric acid. Besides this, the bottom of the boat was covered with a dark gray incrustation (unaffected by hydrochloric acid) which, during the following oxidation, disappeared and after reduction reappeared. In all these cases quantitative reduction was found to be impossible; it could not be effected even at higher temperatures; there

¹ Classen and Bongartz, *Ber.*, 21, 2900 (1888).

always remained a tiny spot of oxide floating on the molten silvery surface.

Parallel experiments made with the pure tin used in A showed that these phenomena, observed during oxidation and reduction, are due to the impurities in electrolytic tin and are not caused by the hydrogen or oxygen used.

Omitting the first electrolysis, where the produced tin showed, after remelting, a small inexplicable increase, we got from the other 4 a mean value for the impurity of the electrolytic tin, of 0.00021 g. per g. of tin, which would have the effect of increasing the atomic weight by +0.08.

D. Synthesis of Tin Tetrabromide.

The next step in the revision of the atomic weight was the synthesis of tin tetrabromide from pure tin and bromine prepared by Brauner's method, described later.

The first experiment, involving the synthesis and weighing of the stannic bromide, when the excess of bromine had been distilled off, gave a negative result, owing to the volatility of stannic bromide.

The second experiment was carried out in a Landolt tube, excess of bromine being determined by titration, with 0.05 *N* sodium thiosulfate solution. A piece of tin foil was placed in one arm of the Landolt tube, in the other was placed a glass bulb containing a weighed quantity of bromine, which had been introduced into the bulb under a bell-jar by repeated alternate evacuation and introduction of pure dry air. However, this experiment also gave negative results, because of difficulties caused by the titration of the excess of bromine.

E. Analysis of the Tetrabromide.

Preliminary Determination of the Atomic Weight.

The best and most reliable method for atomic weight determinations has always proved to be the analysis of compounds with halogens, as elaborated by Richards and his co-workers. Dumas had used tin tetrachloride for atomic weight determinations, but his method did not prevent hydrolysis from taking place during the titration of the silver excess with sodium chloride solution and neglected thus an occlusion of silver nitrate by liberated stannic acid. Moreover, the value obtained was unfavorably affected by the use of impure silver and by the mixing of highly concentrated solutions.

In the case of tin, the chloride or bromide alone is to be considered. The chloride perhaps would be more suitable, since it can be obtained very pure, because it can be distilled without decomposition, and is less easily hydrolyzed than the bromide. On the other hand, the preparation of bromide is simpler (pure dry bromine being easily obtainable), the tetrabromide shows less tendency to form the oxy-salt, and the formation

of dibromide does not take place. The bromide is far more stable at higher temperatures, and as it solidifies below 30° , it can be handled as a crystalline mass. For these reasons the bromide was chosen for this work.

Preparation of Pure Substances.

Tin.—Pure tin was rolled out into thin foil which was then cleaned with sea-sand, washed in pure benzene, in alcohol, and finally in distilled water, and dried at 145° .

Bromine was prepared by Brauner's method, namely by liberating bromine from pure potassium bromide by means of chromic acid and collecting under water. The bromine thus obtained was shaken with water, purified from chlorine and iodine by rectification over a mixture of water, potassium bromide and zinc oxide, and dried by shaking with calcium bromide and calcium oxide, the last traces of water being removed by phosphorus pentoxide. The dry bromine was then redistilled in a glass apparatus, connections having been made with air-tight joints.

Tin Tetrabromide.—The preparation of this substance was accomplished in a suitably adjusted Lorenz's¹ apparatus. The whole apparatus was of glass, single parts being sealed together or connected by air-tight ground joints.

The single parts, as well as the whole apparatus, were thoroughly steamed out in a room perfectly free from hydrogen chloride. Then through the whole apparatus there was passed dry air supplied by a water pump and purified by washing first with alkaline permanganate solution, passing over conc. sulfuric acid, then through 2 tubes filled with melted potassium hydroxide and finally through 2 tubes containing phosphorus pentoxide and glass beads.

Pieces of the purified tin foil were then placed into the chief reaction bottle R and the whole system finally dried by repeated evacuation over tubes with phosphorus pentoxide and calcium bromide. Bromine from Bottle A distilled into Bottle B, which was provided with an air-tight tap² and ended in a capillary in the reaction Bottle R. In this way the flow of bromine was so regulated as to prevent an overheating of the reaction bottle as well as to keep the bottle free (as far as possible) from bromine vapors during the operation. During the reaction of bromine on tin Bottle R was kept shut off from the remaining parts by an air-tight glass Stopcock 2; while communication with outside air was made through a drying tube system, similar to that of Bottle D, containing Tube M, with calcium bromide and N, with calcium chloride. The reac-

¹ *Z. anorg. Chem.*, 9, 365 (1895).

² The stopcocks were made with long necks and were ground very smooth. They were tested by being connected to a vacuum when it was found that no perceptible leakage occurred during an hour and a half. No lubricant was used.

tion started violently, sparks being formed at the points of contact of bromine with tin, but became moderate as more tetrabromide was formed and the addition of bromine suitably regulated. The dripping of bromine

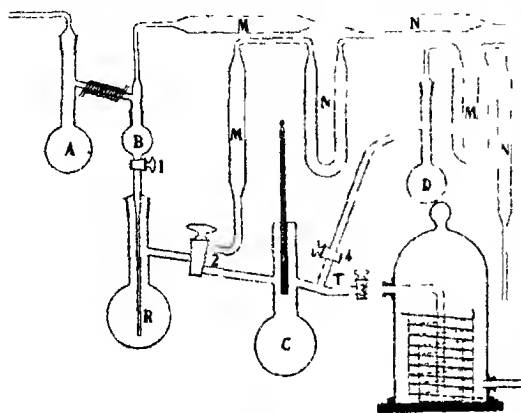


Fig. 1.

was stopped so as to leave some tin uncombined. stopcock connecting with Bottle A and Vessel B and Stopcock 2 were closed. The reaction bottle, containing tin tetrabromide, thus isolated, was warmed. During the warming the slight brownish bromine coloration disappeared and the liquid tetrabromide, colorless and refracting like carbon disulfide,

was distilled through Stopcock 2 into the fraction Bottle C, which was provided with a narrow tube sealed in the neck for thermometer. Then after Stopcock 2 had been closed the distilled portion was again divided into 3 parts. The first part boiling at $200.5-201^{\circ}$, distilled over into the Bottle D (the communication with the bell-jar was cut off by means of Stopcock 3), through the stopcock 4. The middle fraction, with a constant boiling point of 201° , was distilled through Stopcock 3 into a glass beaker placed under the bell. In this beaker were suspended small resistance-glass bulbs, each of which had been weighed and marked. The connection with the glass-bell was made by means of a fine ground stopper to which was sealed a narrow tube extending to the bottom of the glass beaker. In order to keep the tetrabromide liquid, the temperature inside the bell was maintained at 45° by means of an electric oven to which the electric current was conducted through Tubes M and N, terminating in airtight joints.

The bulbs were filled by repeated evacuation and slow admittance of dry pure air (Fig. 2), whereupon the electric current was cut off and the tetrabromide allowed to solidify on cooling. Then the tube T was

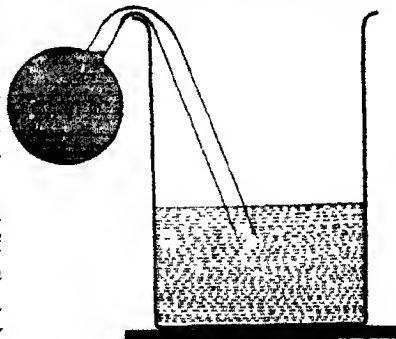


Fig. 2.

cut, the contents of the bell taken out, and every bulb quickly sealed. During this operation the column of solid tin tetrabromide in the necks prevented the air from coming into contact with the inside of the bulbs (Fig. 3). The single bulbs and the corresponding necks were then washed with nitric acid and distilled water and finally dried in desiccators over phosphorus pentoxide.



Fig. 3.

Water.—To the distilled water for ordinary laboratory use alkaline permanganate solution was added and left to stand in sunlight for 2 or 3 months. Then it was distilled through a silica condenser and the middle portion redistilled through a platinum condenser. The middle portion of this distillate was kept in resistance-glass bottles.

Nitric Acid was distilled twice and the middle fraction of the second distillation used.

Tartaric Acid was "purissimum pro analysi" purchased in the open market. Water, nitric acid, tartaric acid were all examined nephelometrically.

Silver.—Material was used which was prepared according to Stas by the reduction of silver chloride with glucose.

All these operations were performed in a room free from hydrogen chloride and hydrogen sulfide.

Weighing was done on a balance made by Nemetz-Vienna of which the sensitivity was adjusted so that the addition of one milligram to a 10-g. load changed the zero position by 10 scale divisions. All weighings were corrected for vacuum, the specific gravity of brass taken as 8.33 that of tin tetrabromide as 3.349, and that of silver as 10.49.

Analysis of Tin Tetrabromide. Series A.

The ratio $\text{SnBr}_4 : 4\text{Ag}$ was determined, the atomic weight of tin being thus directly compared with the fundamental atomic weights of silver and bromine. The weight of tetrabromide was found by weighing the empty bulbs and adding the pieces of glass sealed off. An amount of silver calculated according to the weight of tetrabromide, was weighed and dissolved in a 500 cc. flask provided with a column of bulbs to catch possible splatterings. For the solution of silver 10% nitric acid was used in small excess. All of the silver dissolved overnight without warming; after this the nitrous acid and oxides of nitrogen were expelled by heating and the solution was then diluted through the column of bulbs so as to be less than 0.1 N.

The bulb containing tetrabromide was introduced into a calibrated glass cylinder with a finely ground stopper, then broken under water which contained nitric acid and tartaric acid, and the solution diluted.

Only through this introduction of tartaric acid was it found possible to solve the problem of the revision of the atomic weight of tin. Tartaric acid, even in greatly diluted solutions, keeps tin in solution, probably as a complex stannyl-tartrate ion, which is not precipitated by silver, so that no silver stannate can be formed. The advantage of similar complex compounds has been used in the determinations of the atomic weights of antimony by Cooke and tellurium by Brauner.

Solutions were mixed in a dark room in yellow light. After all of the silver nitrate solution had been poured slowly and with continuous agitation into the cylinder containing the bromide, the cylinder was closed by a glass stopper, put into a cardboard box and strongly shaken, first by hand, then about 4 hours on a shaking machine. After standing overnight the precipitated silver bromide had settled in a fine compact form. Since the solutions were very dilute before mixing, all occlusion was precluded. At the end of 36 hours, when the supernatant liquor was clear, the solution was tested nephelometrically, according to the method elaborated by T. W. Richards.

Analysis No. 1 (trial analysis), 2.11620 g. of SnBr_4 was dissolved in water containing 25 cc. of distilled nitric acid and 3 g. of tartaric acid. This solution was then diluted to 280 cm³. For the preparation in this first trial analysis a quantity of silver nitrate recrystallized several times in the dark was used, corresponding to $\text{Sn} = 118.80$, $1 \text{ c. AgNO}_3 = 3.28050 \text{ g.}$ or reduced to vacuum $= 3.28093 \text{ g.}$ The volume of the silver nitrate solution was 150 cm³, the total volume was 440 cm³. The analysis was then carried out according to the above mentioned method used at Harvard University.

In a similar manner 3 other analyses were made, for which silver was weighed directly. The following results were obtained:

TABLE II.—ANALYSES OF TIN TETRABROMIDE

No. of analysis	SnBr_4 G.	Vacuum cor. G.	Silver G.	$\text{SnBr}_4 : 4\text{Ag}$	Atomic weight
1	2.11620	2.11664	2.08430	1.01551	118.55
2	1.11940	1.11964	1.10206	1.01595	118.73
3	1.97386	1.97428	1.94359	1.01579	118.67
4	2.35420	2.35469	2.31788	1.01588	118.71

Mean of analyses No. 2, 3, 4 = 118.70 ($\text{Ag} = 107.88$, $\text{Br} = 79.916$)

Discussion.

The low value of the trial analysis (with weighing of silver nitrate) would be expected, since the error due to the use of crystals of silver nitrate not 100% pure lowers the result. The mean of the 3 other analyses is 118.70. Stoichiometrically it is of interest that the ratio $\text{SnBr}_4 : 4\text{Ag} = 1.01587 : 1$ is nearly ideal. In these analyses Stas' silver and the sample of tin tetrabromide denoted as A were used. Since the silver, remelted in air, always contains some absorbed oxygen, the true value must be somewhat higher than that found (118.70); however, the error affects only the second decimal.

A final determination will be carried out later with new tin tetrabromide, using silver prepared expressly by Richards' method.

PRAGUE, CZECHOSLOVAKIA.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF BOHEMIAN CHARLES UNIVERSITY OF PRAGUE.]

A REVISION OF THE ATOMIC WEIGHT OF TIN.¹ II.

BY HENRY KREPELKA.

Received February 13, 1920

We have determined in a new and more careful series of trials, the ratio $\text{SnBr}_4 : 4\text{Ag}$ by analysis of newly prepared tetrabromide of tin.

The materials for this purpose were prepared with great care and cleanliness, and chief attention was paid to removing all traces of moisture from the bromine used for the synthesis of the tetrabromide and to keeping the latter in an absolutely dry state. Individual analyses were carried out in the same way as before,² although one profited, of course, by the experience gained in the earlier work. The details follow:

Preparation of New Materials.³

Bromine.—Ordinary bromine was shaken in portions in a separatory funnel containing distilled water, every portion being thus treated 3 times. This bromine was then redistilled from a saturated solution of potassium bromide. The distillate was allowed to drip into a solution of potassium oxalate prepared by neutralizing pure oxalic acid with pure potassium carbonate. The potassium bromide thus obtained was recrystallized 3 times, and its solution was evaporated with a small quantity of potassium dichromate and twice distilled sulfuric acid. The bromine thus set free removed all iodine that may have been present. This evaporation was repeated 3 times. In order to remove organic matter the dry bromide was melted in small quantities in a platinum crucible. From this re-melted bromide, bromine was set free by means of an amount of potassium dichromate and sulfuric acid, such as to leave undecomposed bromide in the distilling flask. The bromine was then redistilled and from a portion of this distillate was prepared the calcium bromide used to dry the remaining part of the bromine, which was then further dried by shaking it with phosphorus pentoxide (twice sublimed in a stream of oxygen), and was afterwards distilled directly into the apparatus in which the synthesis of tetrabromide took place.

Tetrabromide of tin was prepared in the modified Lorenz apparatus. During the preparation the communication with the outside air was ef-

¹ Presented to the Bohemian Academy of Sciences, Prague, 1919.

² B. Brauner and H. Krepelka, *THIS JOURNAL* (preceding paper).

³ The remaining reagents not mentioned here were prepared in the same way as stated in the preliminary work.

fectcd by a drying system (described in the preceding communication) to which were added tubes containing sublimed phosphorus pentoxide.

The course of the reaction showed that both the bromine used and atmosphere of the reaction bottle were absolutely free from moisture, since the first drop of bromine did not at once react with the tin foil—only after 5 minutes did the reaction begin slowly to take place. As soon as the first foil was covered with tetrabromide the reaction became violent and accompanied by such heat that the surrounding pieces of foil were melted into a ball, and the whole reaction bottle had to be quickly cooled.

The tetrabromide obtained was introduced into glass bulbs provided with cone-shaped necks and there sealed. This arrangement removed the difficulties encountered at the same operation during the preliminary work, when the bulbs used had straight necks.

Silver.—750 g. of pure ordinary silver was dissolved in portions in distilled nitric acid (1 : 2) in such a way as to leave a small part of the silver undissolved.

The solution of silver nitrate thus obtained was heated to the boiling point and, after the expulsion of nitrous gases, was filtered. The clear solution, colored pale blue by copper, was allowed to crystallize by evaporation. Silver nitrate thus obtained was fused in a porcelain dish until the melted mass became black. This black substance was dissolved in water and the solution was filtered and allowed to crystallize by evaporation. The crystallization was repeated 3 times. A spectroscopic examination of the last crystals showed only the lead line 3683.62 (intensity 1000), proving thus that all other metals had been removed.

The silver nitrate obtained in this manner was reduced by ammonium formate (prepared from pure formic acid and freshly distilled ammonia) and the reduced silver was washed with distilled water until the Nessler reagent gave no test for ammonia, dried in an electric drying oven at 150° and then melted in a current of pure hydrogen according to the method elaborated by T. W. Richards.¹

Pure hydrogen for this purpose was obtained by the electrolysis of a solution of pure sodium hydroxide prepared from *pure metallic sodium*. The apparatus used consisted of a long U-shaped tube, in one arm of which was evolved oxygen and in the other hydrogen. The arms were long in order to prevent the mixing of the 2 gases. The hydrogen was conducted into a purifying system composed of 2 Richards' washing flasks filled with a saturated solution of silver sulfate, a U-tube containing fused sodium hydroxide, a tube filled with red hot pumice stone covered with platinum and of another U-tube containing fused sodium hydroxide. The individual parts of the apparatus were connected by means of air-tight ground joints.

¹ THIS JOURNAL, 27, 472 (1903).

Grains of remelted silver were etched with dil. nitric acid which had been redistilled, then washed successively in distilled water, ammonia water, and again in distilled water.

The final delicate operation, namely the preparation of small pieces of pure silver for weighing, was carried out in the following manner. The greater portion of the silver buttons was cut up into small pieces on a slab of pure silver with a sharp steel chisel—the pieces were then etched and washed as above. The remaining grains were rolled between clean steel rollers in such a way that after each passing through the roller the silver was etched and washed in order to remove any trace of iron which it might have acquired. The silver foil was then cut by scissors into small pieces, which were then etched and washed as before.

Weighing was done on the same balance as in the preliminary work, but not until after the weights had been tested and corrected.

Six analyses were made in this series and the following results were obtained:

No of analysis.	No of bulb	SnBr ₄ G	Corr for vacuum G	Silver corr for vacuum G.	SnBr ₄ 4Ag	At wt.	Difference from the mean.
1 ..	19	5 11681	5.11788	5 03796	1 01586	118 702	0.003
2	8	2 46823	2 46875	2.43035	1 01580	118.674	+0.023
3.....	9	0 99489	0 99510	0 97961	1 01581	118.679	+0.020
4	18	1 69798	1 69834	1 67172	1 01592	118.727	—0.028
5.	21	3 54191	3 54265	3 48737	1.01585	118 697	+0.002
6	15	3 82100	3 82180	3 76199	1 01590	118 717	—0.018
Mean, 1 01586						118 699	±0.016
Maximum =						118 727	
Minimum =						118.674	
Difference =						0.053	

Discussion.—The mean value from 6 determinations is 118.699 (± 0.016). The maximum figure, 118.727, found only once, was arrived at by the analysis of Bulb No. 18, which was filled as far as to the neck. The minimum was 118 674 and this was the result of the analysis of Bulb No. 8, likewise filled up to the neck. The maximum difference between the highest and lowest values is thus 0 053. The mean value of all 6 ratios, SnBr₄ : 4Ag, is 1.01586. The only probable source of error of this series of analyses appears to have been the space in the necks of the bulbs not filled with tetrabromide.

The agreement of the resulting mean value of the atomic weight of this series of analyses with the mean value of the preliminary determination increases the probability of this figure, and supports the value of the atomic weight of tin, 118.699 (118.70), as determined by Briscoe¹ and by Bax-

¹ *J. Chem. Soc.*, 107, 76 (1915).

ter and Starkweather.¹ This value has been accepted by the International Committee on Atomic Weights.

In conclusion I wish to express my gratitude to The Bohemian Academy of Arts and Sciences in Prague, with whose financial support this work was carried out. I am also obliged to Professors Dr. B. Brauner and Dr. Sterba-Böhm for their valuable advice as well as to Dr. Sveda for his kind assistance.

WOLCOTT GIBBS MEMORIAL LABORATORY,
CAMBRIDGE, MASS

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF LEAD FROM A JAPANESE RADIO-ACTIVE MINERAL.

BY THEODORE W. RICHARDS AND JITSUSABURO SAMESHIMA

Received February 14, 1920

The lead used in this work came from Hokuto, Formosa, Japan, and was separated from a crystalline mineral crust containing lead and barium² which had been formed in the bottom of a hot spring. According to Hayakawa and Nakano³ this mixture of minerals contains (besides cerium and lanthanum) some radioactive elements, namely, ionium, polonium and radium, but no uranium. With their apparatus, however, they were unable to discover radioactivity in the lead chloride obtained from it.

About 10 g. of metallic lead obtained from this specimen was dissolved in pure nitric acid and the lead nitrate was recrystallized several times and then converted into chloride by freshly distilled pure hydrochloric acid. The lead chloride was recrystallized 4 times by dissolving the crystals in hot water in a quartz dish and adding hydrochloric acid. Before the last crystallization the hot solution of chloride was filtered through a Gooch-Munroe crucible. Owing to the small amount of material, no further purification was attempted. This lead chloride was then used for the determination of the atomic weight of lead.

The ordinary lead used for comparison was obtained from lead acetate, converted into chloride and recrystallized 5 times in the same manner as the Japanese lead.

The method of analysis was similar to that already often described⁴ in other papers. Moist crystals of lead chloride (after washing the last crop with pure water) were transferred directly into a platinum boat which

¹ *Proc. Nat. Acad. Sci.*, 2, 718 (1916).

² Okamoto, *Beitr. Mineral. Japan*, 4, 178 (1912)

³ Okamoto, *J. Geol. Soc. Tokyo*, 18, 19 (1911); Hayakawa and Nakano, *Z. anorg. Chem.*, 78, 183 (1912).

⁴ Barter and Wilson, *Proc. Am. Acad.*, 43, 363 (1907); Richards and Lambert, *This Journal*, 36, 1335 (1914); Richards and Wadsworth, *ibid.*, 38, 2613 (1916); Richards and Hall, *ibid.*, 39, 536 (1917).

had been previously weighed. By this procedure handling and danger of accidental introduction of dust were minimized. The boat was kept in a desiccator until the crystals were dry, then brought into the tube of the "bottling apparatus," fused in a current of pure dry hydrogen chloride and weighed. The salt was dissolved in water containing a drop of pure nitric acid, and no black insoluble residue remained suspended in the solution.

The chlorine contained in this solution was precipitated in the usual manner by its approximately calculated equivalent of silver. The attainment of the exact equivalence between the silver and the chlorine was effected by the addition of one or the other and tested in the nephelometer in the customary way.

All the weighings were reduced to the vacuum standard, the correction for which was calculated from the density of the substances and that of the brass weights. All precautions usual in this sort of work were maintained.

Because of the small amount of the material, the same specimen of Japanese lead salt was used in each analysis. After the first determination was finished, a slight excess of hydrochloric acid was added to the filtrate from the silver chloride in order to remove the last traces of silver; and the supernatant liquid was filtered, evaporated in a quartz dish to small volume and filtered again. This solution was mixed with the purest mother liquor from which the previously used crystals of lead chloride had been deposited, and evaporation was continued until most of the chloride was deposited as crystals. The product was recrystallized from hot water, and then used for the second determination of the atomic weight. A similar treatment intervened between the second and third experiments. One analysis, being defective in execution, was rejected. The parallel determinations made with ordinary lead show that the details of procedure had been adequate, since the result agrees sufficiently well with the more extended and elaborate work of others.

The results obtained were as follows: (The atomic weights of silver and chlorine being taken as 107.88 and 35.46, respectively):

THE ATOMIC WEIGHT OF LEAD.				
From the Ratio, 2 Ag : PbCl ₂ .				
	Corrected wt of fused PbCl ₂	Corrected wt. Equivalent Ag	Ratio PbCl ₂ : Ag.	Atomic weight.
Ordinary lead	3.13929	2 43553	1.28895	207.185
	3.09476	2 40100	1.28894	207.183
Average,				207.184
Japanese lead	2.16756	1.68212	1.28859	207.11
First	1.14536	0.88881	1.28864	207.12
determination	1 34496	1.04358	1.28879	207.15
Average,				207.13

The fact that the latter 3 analyses show a progressive increase in the value of the atomic weight suggests the possibility that the degree of purity of the 3 preparations might have progressively changed. Nevertheless, since from the method of crystallization they should have been essentially alike, the appearance of a march in the figures is probably fortuitous. In any case no claim can be made for great accuracy in the result, because the amount of crude material was not sufficient for work of the highest precision. In spite of this lack, the outcome serves its purpose, for it shows that the atomic weight of this lead from a Japanese radioactive spring is not far from that of ordinary lead. Probably it is chiefly ordinary lead, with perhaps not over 5 % of isotope of lower atomic weight. The result coincides well with the fact, reported by Hayakawa and Nakano,¹ that the lead chloride shows but little if any radioactivity. The quantity of the metallic lead obtained was too small to determine a trustworthy value for its density.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

TRIATOMIC HYDROGEN.

BY GERALD L. WENDT AND ROBERT S. LANDAUER.

Received March 2, 1920

Many years ago Osann² published a series of papers on a reactive variety of hydrogen produced by the electrolysis of dil. sulfuric acid. To this he gave the name of "Ozonwasserstoff" on account of its analogy to Schönbein's ozone which had just been discovered, but without knowledge of its molecular formula. After protracted arguments Löwenthal³ seems to have proved that the reducing action of Osann's gas was due to sulfur dioxide produced from the sulfuric acid. In any case, Osann's work has never been confirmed, though G. Magnus⁴ made persistent efforts to do so. All other known forms of active hydrogen are undoubtedly monatomic, including the ordinary nascent hydrogen and Langmuir's modification⁵ which is produced when a metallic filament is heated in hydrogen at very low pressures.

In 1913, however, Sir J. J. Thomson⁶ published photographs of the

¹ *Loc. cit.*

² *J. prakt. Chem.*, 58, 385 (1853); 61, 500 (1854); 69, 1 (1856); 71, 355 (1857); *Verh. Würzburger phys.-med. Ges.*, Bd. VI; *J. prakt. Chem.*, 66, 102 (1855); 78, 93 (1859); 81, 20 (1860); 92, 210 (1864); *Pogg. Ann.*, 95, 315 (1855); 95, 311 (1855); 97, 327 (1856); 98, 181 (1858); 106, 326 (1859).

³ *J. prakt. Chem.*, 73, 116 (1858).

⁴ *Pogg. Ann.*, 104, 555, Par., 98-110 (1858).

⁵ *THIS JOURNAL*, 34, 1310 (1912); 36, 1708 (1914); 37, 417 (1915).

⁶ *Proc. Roy. Soc. A.*, 89, 1 (1913); "Rays of Positive Electricity," Longmans, Green & Co., 1913.

parabolic traces obtained on a sensitized plate upon which the positively charged particles present in a high vacuum discharge tube had been allowed to impinge after simultaneous electrostatic and magnetic deflection. The position and form of the parabolas revealed the presence of particles having an atomic weight of 3, presumably triatomic molecules of hydrogen. This was later confirmed by Dempster,¹ using the electrical method. Duane and Wendt² showed, in 1917, that when hydrogen is exposed to bombardment of α -particles from radium emanation a contraction in volume ensues, a fact which had been incidentally observed by Usher and which has been recently confirmed by Lind.³ These indications that hydrogen may exist in the ozone form deserve careful study not only because a reactive variety of hydrogen might be of great value when applied to hydrogenation and other reducing reactions, but also because the existence of such a form is not compatible with the older theories of valence. If hydrogen has an indivisible valence of one, no triatomic molecule can be formed. The present conceptions of atomic structure, on the other hand, do permit such a molecule, as Bohr⁴ has recently shown.

In the present research this form of hydrogen has been prepared in several ways, all dependent on gaseous ionization, and has been shown to be chemically very active. Although formed in relatively small quantities by present methods, it is a much stronger reducing agent than ordinary hydrogen, and, as would be expected, it rapidly decomposes into the ordinary variety.

The Preparation of Pure Hydrogen.

The hydrogen was prepared in the familiar zinc amalgam-platinum cell with 8% hydrochloric acid as the electrolyte. This type of cell has been found to deliver very pure hydrogen in numerous atomic weight determinations in the laboratories of T. W. Richards.

In order to prevent contamination of the hydrogen by organic materials, we avoided the use of stopcock grease throughout. The stoppers of the generator and of the purifying towers were surrounded by short lengths of wide rubber tubing, which permitted the entire stopper to be covered with mercury. This arrangement proved to be sufficiently gas-tight. In place of stopcocks, we substituted U-tubes filled with mercury, which could be opened by applying suction through a side tube to withdraw the mercury from the U.

The hydrogen from the generator passed first through 3 Emmerling towers filled with lumps of potassium hydroxide which had been fused with

¹ *Phil. Mag.*, 31, 438 (1916).

² *Phys. Rev.*, 10, 116 (1917).

³ *This Journal*, 41, 545 (1919).

⁴ *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 28, 1 (1919).

a little potassium permanganate to remove organic matter. This freed the gas from the acid spray, chlorine, carbon dioxide, and a large part of its water vapor. Air, which had been dissolved in the acid solution, was next removed by passing the hydrogen through a hard glass tube filled with clean asbestos fibers which had been soaked in chloroplatinic acid solution and ignited to impregnate them with platinum black. The tube was wound with Nichrome ribbon covered with asbestos and was maintained at a red heat by an electric current. The joints between the hard glass and the soft glass of the rest of the system were ground to a close fit and were surrounded by a jacket of glass filled with mercury. This again gave a gas-tight joint without the use of grease. The gas was again dried in 3 towers of potassium hydroxide lumps and passed finally through a U-tube about 45 cm. in length and filled with phosphorus pentoxide, which removed the remaining water vapor.

The hydrogen, after this treatment, could have been contaminated only with nitrogen and the rare gases which might have been dissolved in the acid of the generator. To remove even these as far as possible, we exhausted the whole system by means of a water aspirator to very close to the vapor pressure of the acid solution. Hydrogen was then generated until the pressure reached atmospheric value. After 3 repetitions of this exhaustion, the entire system was swept out by its own hydrogen for 40 hours before the commencement of the actual experiment.

As a further precaution against some unknown impurity in this hydrogen, we made a few experiments with hydrogen derived from the electrolysis of a weak solution of potassium hydroxide containing a little barium hydroxide to remove carbonate. The solution was in a cylindrical vessel and a wide ring of heavy platinum wire formed the anode. Within this hung a smaller glass cylinder tapering at the top and sealed to a glass tube which, in turn, was sealed to the U-tube in place of the previous generator. A strip of platinum gauze sealed into the inner cylinder formed the cathode. The cylinder extended 25 cm. below the level of the cathode and anode in order to prevent contamination by the oxygen liberated at the anode. This hydrogen was purified exactly as in the first case, except that the system could not be exhausted.

The effects observed were obtained with both varieties of hydrogen and equally well with compressed electrolytic hydrogen purchased in tanks and purified in the above purifying system. Most of the later work was done with such hydrogen. The impurities present, with the exception of oxygen, seem to have little effect on the preparation of an active gas. In several experiments the hydrogen was passed through a long coil immersed in liquid air with no change in the observed results.

Activation by Alpha Rays.

One of us, using moderate quantities of radium emanation, presented for the purpose by Dr. William Duane, of the Harvard University Cancer Commission, has shown¹ that when α rays from radium emanation are allowed to ionize pure hydrogen gas, an active form of hydrogen results, which is able to reduce sulfur to hydrogen sulfide, the latter being detected by its blackening lead acetate paper. Similarly, phosphorus was reduced to phosphine, arsenic to arsine, permanganate to manganese dioxide in neutral solution, and to a manganous salt in acid solution. The chemical activity is not due to ions, since an electrostatic field does not remove it. Liquid air, however, condenses or removes the active form. The test papers in Fig. 1 show typical results, the first and third being normal results, while the second was obtained by interposing a coil immersed in liquid air between the exposure of the hydrogen to α rays and its reaction with the sulfur. The active form of hydrogen thus obtained is unstable, since little or no test for it is obtained if more than a minute is allowed to elapse between its activation and its reaction.



Fig. 1

Two questions of fundamental interest remain unanswered by this work—the molecular formula of the active gas and the mechanism of its formation. Is it formed by direct bombardment, that is, by the energetic projection of one molecule or atom into another molecule by the α -rays, or is the activity due to the molecular fragments themselves, or, finally is the active molecule polyatomic and a secondary result of the ionization of the hydrogen? The subsequent work all points to the third of these possibilities.

Activation by the Electrical Discharge in Vacuum.

Assuming that the active variety is an ozone form, the high potential electric discharge in vacuum seemed to offer a feasible method of activation, inasmuch as ozone is readily formed in such a discharge, and R. J. Strutt has recently shown² that nitrogen also is activated on passing through it. Activation by this method would indicate, of course, that no direct bombardment is needed, and that the activity is due either to molecular fragments, to ions, or to secondary products of ionization.

The apparatus we used is shown diagrammatically in Fig. 2. F is the discharge tube, made of Pyrex glass, about 10 cm. in length and 2 cm. in diameter, with ring electrodes of aluminum, platinum, or tungsten. These latter were attached either to the secondary terminals of a large induction coil or to the terminals of a 2,200 volt alternating current trans-

¹ *Phys. Rev.*, 10, 116 (1917).

² *J. Chem. Soc.*, 113, 200 (1918).

former, operated on a 220-volt lighting circuit. The hydrogen entered from the purifying system through the stopcock A and the long, capillary tube B. By this means the speed of the hydrogen stream could be delicately regulated to maintain any desired pressure in the discharge tube. The entire system beyond this point was under reduced pressure produced by a rotary oil pump. The pressure was varied between 2 and 8 cm. in

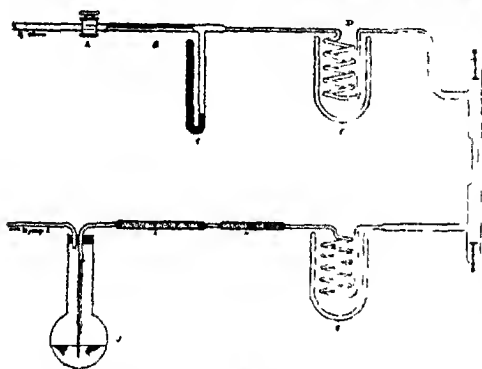


Fig. 2.

the various experiments. After passing through the discharge in a continuous stream the hydrogen passed through a glass coil at G, through a plug of glass wool in H, then over coarsely ground, crystallized sulfur, I, held in place by loosely packed glass wool, and finally through the tube J, in which was suspended a small strip of filter paper, the lower end

of which was dipped in 10% lead acetate solution. The hydrogen was not allowed to pass directly through the solution because of the splashing caused by the rapid stream, but the paper needed to be constantly moistened because the hydrogen had been so thoroughly dried. The gas then passed on through the pump.

Hydrogen was first passed through this apparatus for one hour without the application of the discharge. No blackening of the test paper resulted. Many similar blank runs were made in the course of the work, but in no case was there any indication of sulfide formation when the discharge was not passing. As soon as the discharge was applied, however, sulfide was formed. In many experiments as much sulfide was formed in one minute as had been produced in a run of 8 hours with the α -ray tube. The papers shown in Fig. 3 were typical tests obtained within 3 minutes. Longer runs gave heavy brown precipitates in the lead acetate solution. A blank run was usually made between 2 positive experiments. There is no doubt whatever that the discharge is responsible for the action on the sulfur.

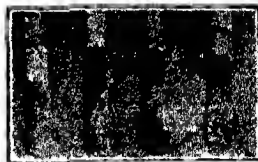


Fig. 3.

In order to exclude the possibility that the action on the sulfur had been due to a slight warming of the latter by the heat of the discharge, either by conduction along the walls or by the hot hydrogen, the coil at G,

was immersed successively in boiling water, an ice-water mixture, calcium chloride-ice mixture (about -20°) and liquid air. There was no apparent difference in the amount of sulfur recorded in any case except the last. As in the experiments with the α -ray tube, liquid air seems to condense out the active gas and there is no action on the sulfur. That the effect is not due to a condensible impurity was shown by interposing a long coil cooled with liquid air at E before the hydrogen entered the discharge tube, an expedient which had no effect on the results obtained. The actual quantity of active gas was always so small, however, that no evidence of its collection in the cooled coil has yet been obtained.

It is not certain that positively or negatively charged molecules or atoms of hydrogen would attack the sulfur, but it was important to show that these were not present. This was first done by interposing between the discharge tube and the sulfur a glass tube one cm. in diameter which had been silvered longitudinally in 2 quarter cylinders. These were connected to the 2 terminals of an 800-volt battery of small dry cells, and should thus have removed the ions completely. This tube had no effect on the activity of the hydrogen. The hydrogen went through the tube rapidly, however, and it was possible that ions were still passing. In order to obtain positive evidence, therefore, a very sensitive electroscope, such as is used for the determination of small quantities of radium emanation, was interposed at that point, represented by F in Fig. 4. To test its sensitiveness a glass tube containing 2 mg. of radium bromide was placed at C and shielded from the rest of the system by the lead blocks D. The "natural leak" of the elec-

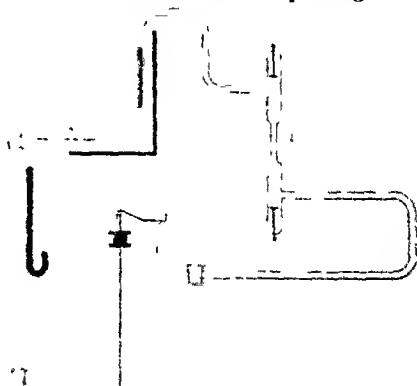


Fig. 4

troscope was 75 minutes per scale division. With the radium in place and the hydrogen passing, but with no discharge, the leaf G fell through one division in 19 minutes. The radium was then removed, the hydrogen was passed at the same rate and pressure as before, but with the discharge passing. The leaf fell through a division in 75 minutes—a leak identical with the natural leak of the instrument, indicating that no ions were passing through. The discharge thus seems to remove all the ions it produces. Indeed, the rate of fall was no greater when the radium was left in place and the discharge passed. The discharge removed the ions produced by

the radium. This is hardly surprising, however, since these form only a minute fraction of the ions present in the discharge itself. These experiments are conclusive evidence that the activity of the hydrogen is not due to ions, for good sulfide tests were obtained in every case.

The number of ions produced in air by the β -rays from one g. of radium is 9×10^{14} and by the γ -rays is at most 13×10^{14} , the sum being 2.2×10^{15} . Only 2 mg. was used, which thus could give 4.4×10^{12} . Since, however, the rays passed through not more than one mm. of hydrogen, 1% of this would far exceed the number of ions actually produced. This is 4.4×10^{10} . If every ion produced a molecule of hydrogen sulfide there should have been 4.4×10^{10} molecules of hydrogen sulfide formed per second, or 8×10^{12} in a run of 3 minutes. Since there are 10^{23} molecules in a cubic centimeter, this is less than 10^{-19} and less than 10^{-18} g., an undetectable quantity. Hence, even had the number of ions detectable by the electroscope been present, they would have been entirely inadequate to give the observed quantity of hydrogen sulfide.

It was important to determine this quantity. A solution of sodium sulfide containing the equivalent of 0.0386 g. of hydrogen sulfide per liter was prepared, and various amounts of it were placed in a small round-bottomed flask inserted in the system in place of the sulfur tube. Dil. hydrochloric acid was added through a dropping funnel while the stream of hydrogen was passing as usual. The solution was boiled to expel all the hydrogen sulfide formed. It was found that one cc. of the sulfide solution was sufficient to give a typical test with the acetate paper. Similar tests were obtained in the actual experiments when hydrogen passed for 3 minutes at the rate of 133 cc. per minute. Hence, 400 cc., i. e., 0.035 g., of hydrogen contained 0.0000386 g. of hydrogen sulfide or 0.000022 g. of combined hydrogen. If we assume the active form to be utilized completely in sulfide formation, as for instance by the reaction $2H_2 + 3S = 3H_2S$, the minimum percentage is $0.000022/0.035$ or 0.006%. Though this determination is not exact, it is evident that the percentage is of the order of 0.01%.

This percentage is confirmed by experiments on the reaction of active hydrogen with nitrogen at atmospheric pressure, which will be described in the next section of this paper.

Activation by the Corona.

Since the activation of hydrogen by α -radiation shows that the active form of this gas is fairly stable at pressures as high as atmospheric, and since the activation by the electric discharge shows that ionization by an electron stream is sufficient to cause the activation, it should be possible to produce the active gas by passing it through a corona tube or through an ordinary ozonizer. This proved to be the case.

Fig. 5 shows diagrammatically the apparatus used. This was devised by Mr. A. C. Grubb, in this laboratory, and was used by him in the activation of nitrogen, as will be described in a paper soon to be published. We are indebted to Mr. Grubb for much of the work on hydrogen at atmospheric pressure. A platinum wire, 0.625 mm. in diameter, was mounted in the axis of the inner tube of an ordinary glass condenser by passing its ends through holes drilled through glass plates and supported by cement. The condenser tube was made of Pyrex glass in order to prevent the electrical puncturing to which soft glass is subject. The condenser jacket was filled with a dilute solution of sulfuric acid which was kept circulating in order to prevent heating. The acid served

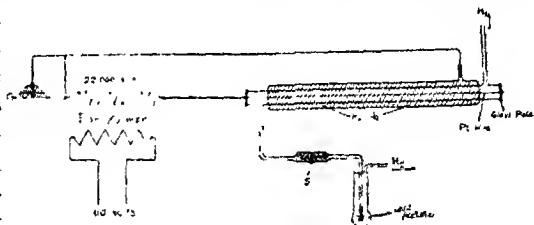


Fig. 5.

as the earthed terminal of the secondary circuit of a high voltage transformer. The latter was constructed by the Thordarson Electric Mfg. Co., of Chicago, and furnished 20,000 volts from a primary current of 110 volts, alternating at 60 cycles per second. The primary current was varied from one to 11 amperes by means of a water resistance. The corona produced by this apparatus was even and continuous. The hydrogen passed through it and thence over sulfur and a lead acetate paper as before.

Hydrogen sulfide was produced. The quantities recorded were, however, smaller than in the case of the vacuum discharge. This may well have been due to the slow rate of passage of the hydrogen in the experiments at atmospheric pressure. The active gas is undoubtedly unstable and reverts to the diatomic modification with such rapidity that not more than a minute must elapse between activation and contact with the sulfur. At reduced pressures, when the hydrogen is being rapidly pumped through the system, the time interval is so small that a large portion of the hydrogen is able to react with the sulfur. The effect at atmospheric pressure is only about $\frac{1}{4}$ as great, due largely to the greater time interval. That this interpretation is correct is shown by testing the effect of varying the velocity of the hydrogen stream.

This is particularly evident in quantitative experiments on the reaction of the active hydrogen with pure nitrogen to form ammonia. Evidence of the formation of ammonia has previously been obtained when a mixture of the component gases was passed through a corona. When pure hydrogen is activated by this method, however, and is then mixed with nitrogen, there is ready formation of ammonia. Nitrogen was

prepared by the usual method of decomposition of ammonium nitrite formed from sodium nitrite and ammonium chloride. It was purified by passage through a long tube of pure reduced copper kept at low red heat and dried by passage over lumps of previously fused potassium hydroxide and a tube of phosphorus pentoxide powder. The chemically prepared nitrogen was later replaced by compressed atmospheric nitrogen obtained from the fractional distillation of liquid air, with no change in the results obtained. The nitrogen was passed at a constant rate of about 5 liters per hour. The hydrogen from the corona tube was mixed with it and the mixed gases were immediately passed through a small absorption apparatus designed especially for the maximum absorption of a small constituent in a minimum quantity of reagent. This absorption tube is shown in Fig. 6.

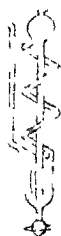


Fig. 6.

It contained about 5 cc. of dil. hydrochloric acid solution, which was later rinsed into a Nessler tube and the quantity of ammonia was determined by the usual method of comparison of the color produced in Nessler's reagent with that produced by standard quantities of ammonium chloride solution.

The gases were passed through for 10 minutes with the corona passing through the hydrogen. The effect of varying the velocity of the hydrogen stream is shown in the following table.

Velocity of H ₂ liters per hour	% of standard NH ₄ Cl solution	% hydrogen combined
0	0	0
3.6	0.85	0.0034
6.0	8.0	0.0192
7.6	5.0	0.0095

The standard ammonium chloride solution contained 0.00001 g. of nitrogen. The percentages are calculated on the assumption that the reaction is $N_2 + 2H_2 = 2NH_3$, which may of course, not be accurate. The percentage activation is of the same order as was observed for the reaction with sulfur in the vacuum experiments. The brief "life" of the active form is shown by the marked increase at higher velocities. In the experiment at zero velocity the corona was passed for 10 minutes through static hydrogen and this was then rapidly swept out and mixed with nitrogen. Decomposition was complete before the nitrogen could react. The highest velocity used was more than the optimum. Since the volume of the corona tube was 80 cc. and this velocity is 8 liters per hour, it seems that the equilibrium concentration of the active gas is not reached in this corona tube in less than one minute. The amount of activation in the corona is of the same order of magnitude as in the vacuum discharge, and at the optimum velocity is somewhat higher. Another

point worthy of note is that little and perhaps no water vapor is needed for the ammonia reaction, as both gases were well, though not perfectly, dried before use. Less thorough drying did not affect the results.

Activation by Schumann Light.

Although hydrogen is extremely transparent to light even in the extreme ultra-violet, Lyman¹ has found some evidence that at wave lengths of 1300 Å and 1600 Å there is absorption, which may, however, be due to impurities. If hydrogen does absorb in this region, the ionization produced should give rise to the active variety of hydrogen. Conversely, the formation of active hydrogen by Schumann light would be definite evidence that one or both of the absorption bands observed by Lyman are due to hydrogen itself, and not to impurities. All attempts to activate hydrogen by this means, however, were unsuccessful.

The source of the light was the hydrogen spectrum produced at a gas pressure of about 7 cm. in a tube of fused quartz by an electrical discharge from a 2200-volt alternating current transformer. The tube was provided at one end with a thin window of clear transparent fluorite. Some specimens of this material are transparent to waves as short as λ 1230 Å. The window appeared perfectly clear and colorless, but its absorption was not measured. The entire tube was immersed in cold water to prevent heating, which accentuates the visible line spectrum of hydrogen at the expense of the shorter wave lengths. The spectrum tube was not sealed off, but was kept connected to the hydrogen supply and to a vacuum pump, so that the pressure could be maintained constant and independent of the heating effect of the current.

A glass tube 3 mm. in diameter was attached by means of a ground joint to the end of the spectrum tube holding the window in such a manner that its axis and that of the spectrum tube formed one straight line. Hydrogen at atmospheric pressure passed through this tube for a distance of 10 cm. and then, after passing a right angle bend, encountered the sulfur as in all other experiments. Continuous runs extending over 8 hours showed no trace of sulfide formation. This indicates that the fluorite was not sufficiently transparent or that the hydrogen does not absorb the Schumann light or that being absorbed, no active hydrogen is formed. If the last is true it is important evidence on the mechanism of the formation of the active molecule. Further work is in progress to evaluate these possibilities.

The Molecular Formula.

Ions.—While there is no reason at present for supposing that gaseous ions may not have some chemical activity and that the reactions observed may, therefore, be due to a reaction of the charged atoms or molecules, the

¹ "Spectroscopy of the Extreme Ultra-violet," Longmans, Green & Co., 1914, p. 70.

experimental evidence is conclusive that no ions are present in the reacting gas. A heavy plug of glass wool, which is ordinarily very effective in removing ions, does not reduce the chemical action. Neither does passage of the gas through an electrostatic field of several hundred volts per centimeter. Finally, the absence of any effect on a sensitive gold leaf electroscope by the strongly reducing gas eliminates all possibility of ionic action.

Atomic Hydrogen.—If, then, the active form of hydrogen is an uncharged molecule, it must be either monatomic or polyatomic. All its properties point to the latter. It is well known that nascent hydrogen, which is probably monatomic, exists only momentarily, while this gas persists for minutes. The ability to pass without sensible weakening through a plug of glass wool is hardly to be expected of atomic hydrogen. The fact that several easily reducible organic dyes are not affected by this gas also argues against a monatomic formula. Finally, Langmuir's active modification is almost certainly monatomic, and is quite distinct from the present gas in many of its properties.

Langmuir's active hydrogen¹ is produced when the diatomic molecule is dissociated into atoms by contact with a metallic filament heated above 1300° K or by evaporation of the atoms dissolved in the metal when that temperature is reached. From calculations of the heat loss of the wires Langmuir calculates the degree of dissociation of hydrogen into atoms as 0.0033 at 2000° K and 0.34 at a temperature of 3500° K. This hydrogen is very reactive, and is destroyed at room temperatures by oxygen or by phosphorus vapor. It reduces rapidly the layers of tungsten and of platinum oxides which occur within electric lighting bulbs. It persists for hours when the pressure is below 0.02 mm. of mercury, but recombines with great speed in the presence of excess hydrogen. It is not detectable at higher pressure. Perhaps the most marked characteristic of this form is its strong adsorption by glass surfaces, especially by glass wool. Freeman² has shown that while it will diffuse through side tubes sealed on the filament bulb, it cannot be found in the side tube if a plug of glass wool is placed at the joint. Hence, the relative stability at atmospheric pressure and the ready passage through glass wool distinguish the new form from this one.

Contraction in Volume.—Positive evidence for a polyatomic molecule is furnished by the contraction in volume now observed by many experimenters when hydrogen is ionized. In the work with α -rays it was shown that a contraction of 3 mm. in 760 was obtained when pure hydrogen was bombarded by α -rays. In a bulb of 5 cc. this meant a contraction of 0.02 cc., a quantity far larger than the volume of niton used. This ex-

¹ *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911), *THIS JOURNAL*, **34**, 860 (1912); **34**, 1310 (1912), **36**, 1706 (1914), **37**, 417 (1915).

² *THIS JOURNAL*, **35**, 927 (1913).

cluded the supposition that the α -rays had driven hydrogen into the walls of the bulb, for it would have been necessary for each α -particle thus to drive many thousands of hydrogen atoms. There remained the possibility that the active hydrogen was reacting with the mercury in the manometer tube, though this was a $\frac{1}{2}$ mm. capillary about 15 cm. long (X, Fig. 7). This improbable hypothesis was excluded by the fact that the original volume of hydrogen was reformed when the niton was withdrawn from the α -ray bulb K, into the bulb N, and reformed at a rate which corresponded with the decay of the powerful α -radiator, radium C, which had, of course, been deposited in the bulb K, by the niton. Lind¹ has recently confirmed this decrease of pressure in hydrogen under the action of α -rays as well as the attack of the active hydrogen on the mercury to form a hydride which is readily decomposed on heating. In his work, however, much mercury was exposed to a mixture of hydrogen with niton, and chemical action on the mercury alone may account for the contraction.

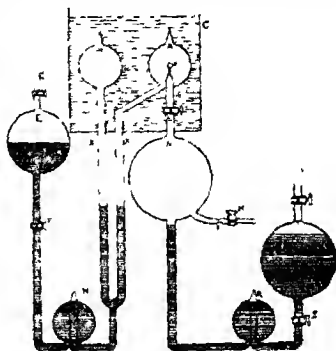


Fig. 7.

Usher² attempted to synthesize ammonia by exposing a mixture of nitrogen and hydrogen to the action of α -rays from niton mixed with the 2 gases. Using, in one experiment, 1.602 cc., he observed a contraction of 0.24 cc., but only 0.006 cc. of ammonia had been formed. Analysis showed that the nitrogen was still present intact, but that nearly a quarter of a cubic centimeter of hydrogen had "ceased to exert any pressure." Since it could not have been projected through the heavy glass walls, he pulverized and heated the latter, but regained thus only 0.06 cc. He left the problem in this stage with the remark that it "is probably much more complicated than it at first sight appears." It is now evident that the observed contraction was due to the formation either of larger molecules of hydrogen or of mercury hydride.

We have repeated Usher's work with the modification that the niton was contained in a small α -ray bulb within the reaction bulb, and that mercury was removed so far as possible by exposing only a very small surface of it in a very fine capillary about 15 cm. distant from the mass of hydrogen and removed from the direct action of α -rays, as shown in Fig 7. Forty cc. suffered a contraction of 0.2 cc., but less than 0.013 cc. of ammonia was found. It is noteworthy that though the possibility of reac-

¹ THIS JOURNAL, 41, 545 (1919).

² J. Chem. Soc., 97, 400 (1909).

tion with mercury was reduced to a very small fraction of Usher's value, the order of contraction is about the same, indicating a real contraction of the hydrogen.

Collie and Patterson¹ have obtained a similar effect in sparking hydrogen under reduced pressure. In one experiment 3.6 cc. out of 4.6 cc. "apparently disappeared" when sparked for 6 hours in a tube with copper or aluminum electrodes at less than one mm. pressure. Here a reaction of the hydrogen with the electrodes is not excluded, although the general tendency under such conditions is for the electrodes to lose any gases they contain. Volume measurements were made by withdrawing the hydrogen from the tube.

Chattock and Tyndall² have also noted a definite contraction when pure hydrogen is sparked between a fine platinum point and a metallic plate, the contraction corresponding to about one molecule per ion. This they interpreted to mean that the ion or single electrified atom of hydrogen is absorbed by the metallic electrode on which it is discharged. This interpretation is by no means certain in view of the present work. The quantitative relation between the ionization and the contraction is in striking accord with the simple relation stated by Lind³ for the chemical action of α -rays. In a large number of such reactions the ratio of the number of ions produced and the number of molecules reacting is very close to unity. If such a reaction as $3\text{H}_2 = 2\text{H}_3$ is responsible for Chattock and Tyndall's observation, the fact that a single ion produces such a reaction is of vital importance in determining the mechanism of the reaction, as will be discussed later.

The volume change in the electrical discharge tube is being further studied in this laboratory, to confirm the work of Collie and Patterson and of Chattock and Tyndall. The heat of the discharge causes so great and so irregular an expansion that no results can yet be announced.

Positive Ray Analysis.—Definite evidence of the existence of relatively large quantities of triatomic molecules is furnished, however, by the method of the positive ray analysis. By this method both Sir J. J. Thomson⁴ and A. J. Dempster⁵ have shown that H_3 exists in the vacuum discharge. According to Dempster higher pressures favor the formation of H_3 at the expense of H_2 and H , as would be expected, and in some cases H_3 is actually the major constituent. While positive ray analysis is remote from ordinary chemical technique, it is an admirable method of molecular weight determination. Aston's failure to separate neon into

¹ *Proc. Chem. Soc.*, 29, 22, 217 (1913).

² *Phil. Mag.*, 16, 24 (1908).

³ *J. Phys. Chem.*, 16, 564 (1912); *Le Radium*, 8, 289. (1911).

⁴ *Proc. Roy. Soc.*, 89A, 1 (1913); "Rays of Positive Electricity," Longmans, Green & Co., 1913.

⁵ *Phil. Mag.*, 31, 438 (1916).

2 constituents by diffusion,¹ following Thomson's discovery of 2 neon lines on the positive ray photograph has cast some doubt on this method, which is now removed by W. D. Harkins² separation of chlorine into two isotopes by diffusion simultaneously with Aston's report of 2 chlorine lines in the positive ray "spectrum."³

Chemical Properties.—Finally, the properties of the new gas are precisely those to be expected of an ozone form. It is much more reactive than ordinary hydrogen, yet not as active as nascent hydrogen. Its boiling point is much higher than that of ordinary hydrogen. And it is unstable, for it cannot be detected if more than about a minute is allowed to elapse between the time of its formation and its reaction with a reducible substance

All the evidence obtained, then points to the formation of triatomic hydrogen, perhaps properly called "lyzone," whenever hydrogen is ionized.

The Structure of the Molecule.

The chief theoretical interest of this work lies in the fact that no hydrogen molecule larger than H_2 is possible on the older conception of valence. Heretofore there has been no evidence that demanded more than a unit valence for hydrogen, and our valence system is based on this unit valence. Yet no triatomic ring can be constructed from unit valence bonds. Increasing the valence of hydrogen to 2 is not possible because this valence is so uniformly connected with one Faraday's equivalent. Nor does the centering of 3 unit valence bonds from 3 hydrogen atoms on a central point solve the question, since such an indefinite subdivision of valence is still a subdivision and is not to be countenanced if valence is a matter of unit quantities.

Of the numerous electronic valence hypotheses which have recently come to the assistance of the theory of valence, only one, that of J. Stark,⁴ can picture the triatomic molecule of hydrogen. According to this a valence bond consists of an electron held in position, between the two atoms which it binds, by numerous lines of force extending to the two atoms, and an ordinary single bond really has two such electrons, one arising from each atom. A triatomic ring of monovalent atoms thus requires simply the alternation of atom with electron in a 6 membered ring. The picture is not convincing, both on physical and on chemical considerations.

There remain the modern fundamental reconstructions of our conceptions of atomic structure, in particular the Rutherford atom on the basis

¹ Private communication, May 5, 1919.

² *Science*, 51, 289 (Mar. 19, 1920).

³ *Nature*, 104, 393 (1919).

⁴ *Jahr. Radioakt. Elektronik.*, 9, 15 (1912).

of which both Bohr¹ and Crehore² have predicted the possibility of the existence of a fairly stable triatomic molecule of hydrogen. Recently Bohr³ has discussed the structure of this molecule, which he gives as a system of 3 electrons rotating at equal angular intervals in a circular orbit, the 3 nuclei being placed, respectively, at the center of the orbit and at 2 points on the axis equidistant from the center. Such a structure is consistent with all that is known on atomic structure and on valence.

Triatomic hydrogen furnishes definite chemical evidence, if not of this structure, then at least of the need for considering valence on the basis of the new knowledge of subatomic phenomena. If it is not a confirmation of present atomic structures, it does demonstrate the inadequacy of past analysis and nomenclature.

The Mechanism of Formation.

Lind⁴ accounted for the formation of ozone from oxygen by the decomposition of cluster ions. He found that each ion produced by α -rays causes the formation of one molecule of ozone. Chattock and Tyndall made a similar observation for hydrogen in the electric spark. Lind found, indeed, that practically all the known gaseous reactions caused by α -rays follow this law closely. It is difficult to picture the mechanism by which a single ion causes a complex reaction such as $3\text{H}_2 = 2\text{H}_2$. Lind supposes that a large "cluster ion" is at once formed by the adhesion of neutral molecules to the original ion and that this breaks down when the charge is neutralized into diatomic molecules and one triatomic molecule, presupposing thus a general loosening of the valence bonds in the cluster ion.

While this explanation accounts for the observed facts, recent evidence seems to prove that cluster ions do not exist. The cluster ion hypothesis was devised originally to account for the extremely low mobility of gaseous ions in traveling through gases. This mobility is now accounted for, however, by the retardation of the ion in its path through the gas by virtue of its attraction for other molecules and the increased number of collisions it therefore suffers without actually attaching itself to the molecules. The work of Loeb⁵ and of Wellisch⁶ shows that if cluster ions exist they do not break up even when traveling under electrical potentials that merge into the potentials necessary for ionization by collision. It is impossible to attribute to them a greater stability than that of ordinary neutral molecules, however, and it thus seems clear that gaseous ions remain very small.

¹ *Phil. Mag.*, **26**, 857 (1913).

² *Ibid.*, **30**, 613 (1915).

³ *Medd. K. Vetenskapsakad. Nobelinst.*, **5**, No. 28, 1 (1919).

⁴ *Am. Chem. J.*, **47**, 397 (1912).

⁵ *Phys. Rev.* **8**, 633 (1916); *J. Franklin Inst.*, **184**, 775 (1917).

⁶ *Am. J. Sci.*, **39**, 583 (1915).

Hence, the explanation of the reaction is to be based rather on the calculations of Bohr,¹ who showed that the usual molecule of hydrogen, consisting of 2 nuclei with 2 electrons rotating in an orbit perpendicular to the line joining the nuclei and equidistant from them, must break up when one of these electrons is removed by any cause. Thus the ionization of hydrogen by any agent inevitably forms 2 free atoms of hydrogen as an intrinsic part of the process of ionization. Since neutral molecules are present in great excess over the free atoms, these latter at once attach themselves to the molecules and form molecules of H_3 with a structure as described in the previous section. This very simple picture accounts for the seemingly complex reaction $3H_2 = 2H_3$, and is in accord with the generalization of Lind. Since the same relation holds experimentally for oxygen as for hydrogen, it follows that the O_2 molecule is similarly unstable and dissociates into atoms whenever it is ionized, with the consequent formation of ozone.

This interpretation is ventured as a rational deduction from the Rutherford theory of the atom, and is by no means free from criticism. It will bear much study, and in particular data are needed for the examination of other reactions on this basis. Fuller consideration of the subject must be delayed until a later time.

Summary.

1. A reactive modification of hydrogen has been produced by several methods, all dependent on gaseous ionization—by the α -rays from radium emanation, by the electrical discharge under reduced pressure, and by the high potential corona at atmospheric pressure. Attempts to produce activation by Schumann light rays failed.

2. This active hydrogen reduces sulfur, arsenic, phosphorus, mercury, nitrogen, and both acid and neutral permanganate. It is condensed or destroyed by liquid air temperatures. It is unstable and reverts to the ordinary form in about a minute. It passes readily through glass wool. It is not less stable at atmospheric pressure than at low pressures.

3. The activity is not due to gaseous ions, and the properties of the active gas are quite different from those of Langmuir's atomic hydrogen. The formation of a polyatomic molecule is indicated by the contraction of the hydrogen when ionized. Positive ray analysis at very low pressures shows a large proportion of triatomic molecules which are undoubtedly the ones responsible for the chemical activity. All the properties of the gas point to its being an ozone form, perhaps properly called "hyzone."

4. The existence of H_3 is applied to the explanation of several previously observed phenomena. The calculations of Bohr on the basis of Rutherford's atom furnish the only valence hypothesis which satisfactorily accounts for its existence.

¹ *Phil. Mag.*, 26, 857 (1913).

5. The mechanism of the formation of triatomic molecules is considered on the basis of the Bohr atom. Stable molecules of hydrogen are perhaps dissociated into free atoms when an electron is removed in the process of ionization, and these atoms attach themselves to neighboring neutral molecules to form triatomic systems.

6. We desire cordially to acknowledge our gratitude for much assistance in this work: to the Director of the Ryerson Physical Laboratory of the University of Chicago for the use of indispensable alternating current and the privileges of that laboratory; to the Research Grant of the American Association for the Advancement of Science for the funds for the construction of the quartz spectrum tube for the Schumann ray investigation; to Professor Stuart Weller, of the University of Chicago, for the gift of an excellent crystal of clear transparent fluorite for the Schumann ray investigation, and to Mr. A. C. Grubb for much of the work on the corona discharge.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE ADSORPTION OF SULFUR DIOXIDE BY THE GEL OF SILICIC ACID.

By JOHN MCGAVACK, JR., AND W. A. PATRICK

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Introduction.

Many investigations of the adsorption of vapors by porous bodies have been made without a satisfactory explanation of the phenomenon being found. The fact that the adsorbing material is not chemically definite but has adsorbent properties dependent upon its method of preparation is not the least of the reasons for apparent lack of agreement both in experimental results and theoretical conclusions. Again, the possibility, and in many cases, the great probability of chemical reaction occurring during the process bring in another factor which is hard to control.

In the investigations carried on in this laboratory during the war it was found necessary to test many types of adsorbents, both as to their specific action against poisonous war gases as well as to their susceptibility towards other vapors and gases. It was realized in the beginning that porous bodies—mere mechanical condensers so to speak—were going to play an important part. Charcoal was brought into use and its protective ability greatly increased by improved methods of preparation. This laboratory focused a good part of its attention upon colloidal substances and gels. The gel of silicic acid, having been previously shown to possess adsorptive properties, received first attention. The main difficulty was its large scale preparation. Up to this time the method

of dialysis, a long and tedious process had been used. This difficulty was overcome and a quick and simple method, of which more will be said later, was developed. A product of high adsorptive power resulted.

This gel is a hard, translucent, porous solid, chemically inert and with proper precautions can be reproduced with definite exactness. Hence it is an ideal substance by which the 2 objectionable features mentioned above might be eliminated. It is true that it always contains a certain amount of water, either combined or adsorbed, but this factor may be kept constant and thus will not interfere with the more important investigation.

Thomas Graham¹ gives the first account of the preparation of silicic acid gel and the fact that it possesses a power of adsorption has been known since that time. Nevertheless, it was not until 25 years later, when van Bemmelen² commenced his lengthy and important experiments, that this property was investigated more thoroughly. This author made an exhaustive study of the hydration and dehydration of the gel in all cases, showing that these two curves did not follow the same path. This hysteresis will be taken up further on in the paper.

Zsigmondy³ became interested in this substance and has published several articles on its structure, data for which were obtained chiefly from ultramicroscopic investigations.

Anderson,⁴ working in Zsigmondy's laboratory, studied the systems, gel-water, gel-alcohol, gel-benzene. That is, he determined the equilibrium weight of each substance adsorbed per gram of gel at points corresponding to different pressures of the material adsorbed. Like that of van Bemmelen, the curve obtained by emptying the pores did not coincide with that observed when they were being filled, although the difference between the 2 paths was by no means as great as in the earlier work. It may also be mentioned that while van Bemmelen worked entirely under normal atmospheric pressure Anderson, on the other hand, did his work under a vacuum produced by the means of a high grade oil pump.

Patrick⁵ was the first investigator of gas adsorption by this substance. He measured the amount of carbon dioxide, sulfur dioxide and ammonia adsorbed by this gel at different pressures for a number of different temperatures. He did not attempt to study the reverse adsorption path, nor did he use samples of the material containing different water content.

¹ T. Graham, *Phil. Trans.*, 151, 183-224 (1861); also *Ann.*, 121, 1-77 (1862); *Proc. Roy. Soc.*, 1864.

² J. M. van Bemmelen, *Z. anorg. Chem.*, 13, 233-356 (1896); "Die Adsorption," p. 196 (1910).

³ Zsigmondy, *Z. anorg. Chem.*, 71, 356 (1911)

⁴ Anderson, "Inaugural Dissertation," Göttingen, 1914.

⁵ W. A. Patrick, "Inaugural Dissertation," Göttingen, 1914. See also *Koll. Z.*, 13-14.

The purpose of the present work may now be stated more clearly: to investigate the effect of different water content of the gel upon its adsorptive powers; to obtain measurements where temperature control and complete exhaustion could be more rigidly maintained than heretofore; and by using an inert body to interpret, if possible, the mechanism by which this phenomenon adsorption occurs

Apparatus.

The apparatus used in these measurements is shown in Fig. 1. In general outline it is similar to that used by Homfray¹ in her work on charcoal and later by Patrick, in the original investigation of gas adsorption by silica gel. The essential parts are the gas container A, the gas buret B, the adsorption bulb C and the manometer D. These parts were all sealed together and mounted inside of a constant temperature bath about which more will be said later. The gas container was a steel cylinder filled

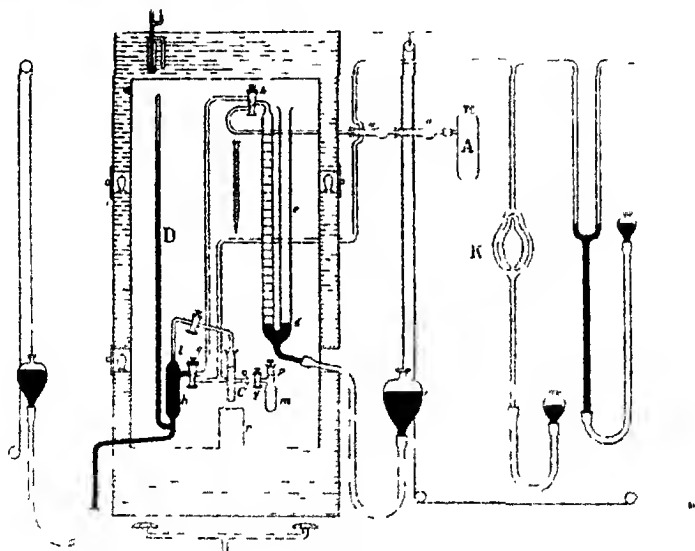


Fig 1

with liquid sulfur dioxide, the outlet of which was controlled by a sensitive valve. This was connected to the gas buret by means of drying tubes *a* and *a'*, containing calcium chloride and phosphorus pentoxide, respectively, and the 3-way mercury stopcock *b*. In order to fill the buret the stopcock *b* was opened to the adsorption apparatus and the mercury bulb *c* raised until all the air was forced out of the buret. The cock was then opened to the gas container and the mercury well *c* was lowered.

¹ *Z. phys. Chem.*, 74, 129 (1910).

Opening the cock *b* to the adsorption part of the mercury was again raised. This operation, repeated several times, removed a larger part of the air. To remove the last traces of air the bulb was lowered just so the mercury stood at the level *d* in the buret. The cock *b* was then opened to the gas container A and sulfur dioxide was allowed to sweep out the whole system for a considerable period of time. The exit tube from *b* was also swept out in a similar manner.

The gas buret B consisted of a graduated pipet connected by a U-joint to another tube, *e*, of the same bore, which served as an open manometer. This buret was recalibrated, mercury being used and the operation being carried out in a 30° constant temperature bath. As with most gases, all gas volumes were measured at this temperature, and if the temperature difference was less than 10°, no correction for glass expansion was deemed necessary. To determine the amount of gas introduced, the mercury in the two arms of the buret was leveled, this balance being adjusted by means of a very sensitive gear arrangement which enabled the reservoir C to be raised or lowered a small fraction of a millimeter, the correct position being ascertained by means of the cathetometer telescope. The reading of the cathetometer vernier, calibrated directly into 0.01 mm. divisions, was then taken. In like manner another reading was made after the gas introduction. By reference to the calibration curve these readings were transferred into cc. and were then corrected to standard conditions, 760 mm. and 0°. As the height of one mm. was equivalent to 0.19 cc. and as duplicate settings of the cathetometer could be made within 0.03 mm. the maximum error in reading gas volumes was 0.005 cc. As the adsorption proved to be considerable the cc. readings are given only to the second decimal place.

The gas buret was connected by a glass tube of small bore to the 3-way stopcock *g*, which in turn led to the expansion bulb *h*. This part of the apparatus had a capacity of approximately 100 cc. and served as a precaution against too hasty introduction of the gas.

The adsorption container C was connected to the expansion bulb by glass tubing and a ground glass joint protected by a mercury seal. The volume of this bulb together with that part of the connecting tube above the mark was obtained by introducing a known volume of dry air and measuring the pressure developed. Measurements with different volumes showed close agreement and a mean of these values was used for calculation purposes.

The manometer needs no special mention except that it was found desirable to have its bore identical with the bore at *l*. In the apparatus first used this was not the case and a constant correction for capillary depression was necessitated. Pressure readings were also made with the cathetom-

eter and hence all such readings are accurate to within 0.03 mm. The mercury well controlling the manometer was worked by a sensitive ratchet.

In order to study the curve formed while the pores were being emptied the bulb *m* was added by means of the ground glass joint *o*. This served as a holder for granulated soda lime which was introduced through the mercury-sealed ground glass joint *p*. The stopcock *q* maintained a vacuum in this vessel when removed from the apparatus for the purpose of weighing. The electric furnace *r*, previously calibrated, was used to heat the gel to the required temperature during evacuation.

The whole apparatus was enclosed in a completely water jacketed air bath. Three gas burners under the bottom furnished rough heating adjustment, while a system of 8 carbon lamps, inserted in different sections of the water compartments and controlled by relays and a sensitive toluene-mercury regulator, procured very close temperature control. This bath was used by Morse and his co-workers in their measurement of osmotic pressure at high temperatures and hence is described elsewhere¹ in the literature. Suffice it to say that by means of this bath the temperature was maintained constant for any length of time with a maximum fluctuation of less than 0.05°.

In all of the work a vacuum was maintained by using in series a rotary oil pump and a Gaede high-vacuum mercury pump, both manufactured by E. Leybold. A MacLeod gage, K, served to determine when evacuation was complete, such being considered the case when the mercury threads in the gage became level.

Materials.

All the mercury used in this investigation, that for traps, buret, manometer and gage, was thoroughly cleaned and purified. This was accomplished by first allowing it, in a state of very fine subdivision, to fall through 2.4 meters of dil. nitric acid for 5 or 6 times, washing with distilled water, then caustic soda, and finally with distilled water. After drying it was redistilled *in vacuo*.

The rubber tubing used to connect the mercury wells to the remaining part of the apparatus was soaked for 24 hours in dil. sodium hydroxide solution in order to remove sulfur present. This precaution prevented premature fouling of the mercury.

The sulfur dioxide used was that found in the trade and was taken directly from its metal cylinder—a method recommended by Travers in his careful work on purification of gases. Of course its purity was first tested. This was done by immersing a 100 cc. inverted buret filled with sodium hydroxide in a sodium hydroxide solution. The buret was now filled with sulfur dioxide from the cylinder, and after a short time was completely absorbed without the appearance of any gas bubble at the top

¹ *Am. Chem. J.*, 42, 29 (1912).

of the buret. Several experiments were also made from a sample obtained from the same cylinder which had been redistilled. No different results were observed. A further check on the purity of this substance was obtained from vapor-pressure measurements. No change in pressure being noticed, no matter how large a volume of gas was introduced. Hence the possibility of presence of oxygen, nitrogen and carbon dioxide, the most likely impurities, was eliminated.

All of the gel used in this investigation was made by the Davis, Patrick and McGavack¹ process. In general this consists in allowing an acid solution and a solution of sodium silicate, both solutions being kept at the proper concentration, to mix under violent agitation. The hydrosol "sets" in 1 to 18 hours, depending upon the temperature and concentration of the solution. When the desired state of firmness is reached the material was washed with city water, the washing being continued until no trace of electrolyte could be detected in the wash water. The material was then dried at 110° *in vacuo* until the water content was reduced to 7 or 8%. By this method a large amount of material was prepared.

The best grade of sodium silicate solution (water glass) furnished by the Philadelphia Quartz Company was used. C. P. hydrochloric was the acid used.

In order to remove dust particles and possible metal impurities the gel was subjected to still more drastic treatment. This was accomplished by saturating it with nitric acid fumes and refluxing with C. P. conc. nitric acid for 12 hours. The material was then washed thoroughly by decantation from distilled water over a period of 4 days. This part of the operation cannot be hurried or accelerated by increasing the amount of water as the rate of diffusion from the pores of the gel is very slow. The material was then dried in an air bath at 110°.

As even at 110° a large amount of water (16-24%) still remained in the gel, and as uniform samples of different water content were desired, some arbitrary process had to be employed to standardize the water content. This was accomplished by heating a mass of gel for different periods of time under a vacuum at different temperatures. For instance, Sample *c* was prepared by heating for one hour at 100-120° and for 3 hours at 300°. Sample *d* was heated for one hour at 100-120°, one hour at 300°, and finally 2 hours at 500°—a vacuum of 1 to 5 mm. being maintained in each case during the whole time. This treatment was rigidly held to in the preparation of all samples. The samples were then put in glass-stoppered bottles and these in a sulfuric acid desiccator.

All water determinations were made by heating the gel in a platinum crucible with a blast lamp. This method was applicable, as water was

¹ Reports submitted to the Chemical Warfare Service, a résumé of which will be published in the near future.

the only volatile component. The usual method for obtaining the density of an insoluble (in water) solid was employed, especial care being used to see that all adsorbed air bubbles were removed. Table I gives the experimental results.

TABLE I.—WATER CONTENT AND DENSITY OF DIFFERENT SAMPLES.

Sample	c		d		e		f	
	Water, %	Density	Water, %	Density	Water, %	Density	Water, %	Density
4 79	2 1693		3 53	2 244	2 36	2 25 ^a	7 92	2 123 ^a
4 82	2 1604		3 49	2 236	2 26	,	8 03	
4 90							8 07	
Mean:								
4 87	2 1648		3 51	2 240	2 31		8 01	

^a Calculated from values obtained from *c* and *d*

Isotherms were made at -80° , -54° , -34.4° , -33.4° , 0° , 30° , 40° , 57° , 80° and 100° . For $+30^{\circ}$ and $+40^{\circ}$ the constant temperature bath surrounding the apparatus was used. Solid carbon dioxide contained in a Dewar bulb served for -80° . Liquid ammonia also contained in a Dewar bulb and with an arrangement for variable pressure served for the other low temperatures. The freezing and boiling points of water were used for 0° and 100° , respectively. The vapor of boiling acetone and benzene gave the points 57° and 80° . In no case was the adsorption bulb allowed to dip in the boiling liquid itself but was completely bathed with its vapor. The flask containing this liquid fitted tightly at the top around the adsorption bulb and had openings for a thermometer and also a long glass condenser which avoided the necessity of continually adding liquid. In all cases the remaining part of the apparatus was kept at a constant temperature by means of the constant temperature bath.

The actual temperature points of the 2 low degree experiments were fixed by the aid of the vapor-pressure measurements made on sulfur dioxide by Steele and Bagster.¹ These investigators furnish the only measurements of this constant at low temperatures (-73° to -36°) and when the logarithms of these pressures are plotted against the absolute temperature a fairly straight line results. In the other low temperature runs (Expts. XXVIII and XXIX) a xylene thermometer, calibrated recently (1919) by the U. S. Bureau of Standards, was used. The corrected readings on this thermometer were -33.4° for Expt. XXVIII and -34.4° for Expt. XXIX. The vapor pressures observed in these runs correspond to temperatures -37.8° and -38.8° with reference to the Steele and Bagster results. Regnault,² Pictet³ and Sajot,² however, have measured the vapor pressure of sulfur dioxide from -30 to $+100^{\circ}$. Their results are in good agreement with each other and it is interesting to note that the logarithmic curve plotted

¹ Steele and Bagster, *J. Chem. Soc.*, [2] 97, 2613 (1910)

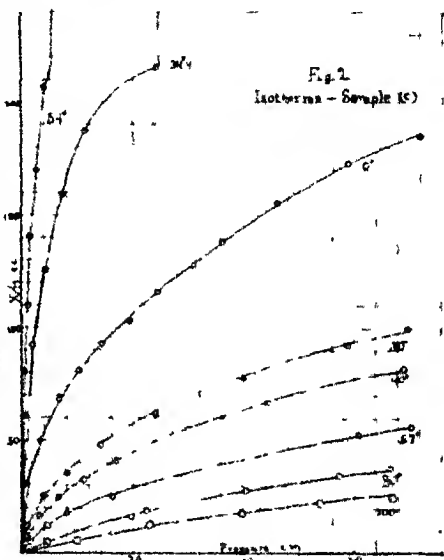
² Results tabulated in Landolt-Börnstein "Tabellen."

from them when extended fixes the temperatures in question at -34° and -35° , respectively, values which seem to be the true ones.

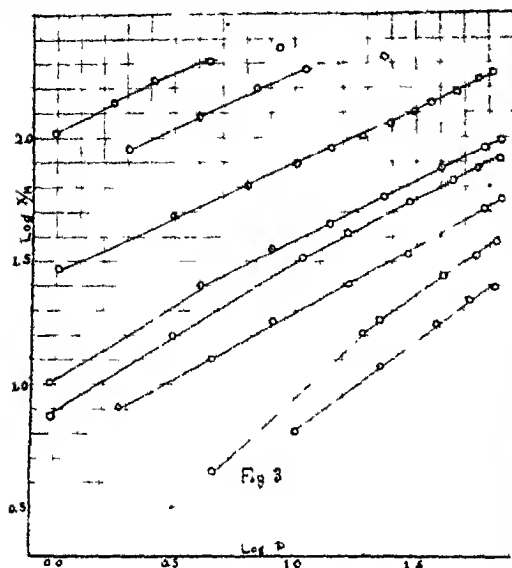
Procedure.

The gel was weighed directly into the adsorption bulb which was then attached to the apparatus. The furnace was put in position and heating and evacuation were commenced at the same time. The temperature and length of heating were governed primarily by a consideration of the water content of the gel. A temperature higher than that used in the preparation of the gel was never employed—this was done so as not to change the amount of water present. The evacuation was continued until the MacLeod gage indicated no pressure. The adsorption bulb was then allowed to come to the temperature desired and the first introduction of gas was made. Amounts of gas such that points might be obtained at 2, 5, 10, 20, 30, 50, 60 and 70 cm. were introduced. After introduction, the mercury level was brought to point *l* (see Fig 1), and by reading this height and also that on the manometer itself, the point where equilibrium was reached could be ascertained easily. The difference between these 2 readings gave the pressure of the system. In the same manner another quantity of gas was introduced and its equilibrium pressure measured. This was continued until atmospheric pressure was reached.

For points on the reverse curves the following method was used. The bulb *m* was partially filled with soda lime granules, Stopcock *q* opened and the whole system thoroughly evacuated. After removing and weighing, the bulb was again attached and the system thoroughly evacuated. The mercury controlling the MacLeod gage was now raised to a point sufficient to cut off its large bulb. Then lowering the mercury in the expansion chamber, *h*, the stopcocks *g* and *q* were opened and gas was given off from the gel. When sufficient had escaped the cock *g* was closed and the mercury in *h* raised to *l*. The pressure gage showed almost instant adsorption by the soda lime, but to avoid any error *q* was left open for an hour in order not to miss the last traces of the gas. It was then closed



and the bulb removed and weighed. The same process was repeated for every point desired. Of course pressure readings were made for every point determined.



All pressure readings were corrected to 0° and all gas volumes to 760 mm. and 0°. The volume of the gas above the gel was calculated each time and subtracted from the amount introduced. Knowing the volume of the bulb C to the mark *l*, also the temperature and pressure, this value was easily calculated from the gas laws. When the bulb and the remaining part of the apparatus were at different temperatures the volume and tem-

perature of each part were considered in the calculation

Experimental.

The results for Sample *c* of the gel are given below. Figs 2 and 3 show these facts graphically

Expt. XII

2.4256 g. (c)					100°	α 1.125	$1/n = 0.745$	
P.	V_0	V_1	X	X/M	log P	log X/M	X/M calc	
105.88	18.24	2.18	16.06	6.62	1.02478	0.82086	6.50	
229.93	33.94	4.74	29.20	12.04	1.36159	1.08063	11.62	
397.00	51.32	8.19	43.13	17.78	1.59879	1.24993	17.43	
544.20	64.57	11.23	53.34	21.99	1.73576	1.34223	22.08	
671.50	73.65	13.85	59.80	24.65	1.82705	1.39182	25.83	

Expt. XIX.

2.6000 g. (c)					80°	α 2.739	$1/n = 0.662$	
P	V_0	V_1	X	X/M	log P	log X/M	$1/n$	
47.00	12.66	1.00	11.66	4.48	0.67210	0.65128	0.448	
192.19	47.60	4.09	43.57	16.73	1.28373	1.22350	0.680	
224.73	53.30	4.78	48.52	18.66	1.35166	1.27091	0.681	
407.88	80.73	8.70	72.03	27.70	1.61053	1.44248	0.678	
575.32	101.09	12.24	88.85	34.17	1.75991	1.53364	0.672	
671.95	111.56	14.29	97.27	37.41	1.82733	1.57299	0.669	

Expt. XX

2 6500 g. (c).		57°.		a 5 755		1/n=0.533.	
P	V _a	V _t	X	X/M	log P	log X/M	1/n.
18 97	17 92	0 42	17 50	6 60	0 27807	0 91954
46.16	34 76	1 03	33 73	12 73	0 66427	1 10483	0.534
81 70	50 42	1 82	48 60	18 34	0 91222	1 26340	0 552
168 84	72 83	3 75	69 08	26 07	1 22747	1 41614	0 534
290.14	97 38	6 45	90 93	34 31	1 46261	1 53542	0 530
615.65	151 75	13 68	138 06	52 10	1 78933	1 71684	0 534
713 50	164 51	15 86	148 65	56 09	1 85339	1 74889	0 533

Expt XVIII

2 600 g. (c)		40°		a 9 755		1/n=0.50647.	
P	V _a	V _t	X	X/M	log P	log X/M	1/n.
9 44	19 72	0 22	19 50	7 50	1 97497	0 87506	0 4560
31 37	43 63	0 72	42 91	16 50	0 49651	1 21748	0 4596
64 77	67 14	1 49	65 65	25 25	0 81137	1 40226	0 5090
110 00	90 05	2 54	87 51	33 66	1 04139	1 52711	0 5165
189 13	112 80	3 90	108 90	41.88	1 22622	1 62201	0 5152
299 78	151 28	6 88	144 40	55 54	1 47680	1 74461	0 5114
448 60	184 95	10 30	174 65	67 17	1 65186	1 82718	0.5072
567 51	208 22	13 04	195 18	75 07	1 75398	1 87547	0.5053
692 20	229 51	15 88	213 63	82 16	1 84023	1 91466	0.5028

Expt XXIII

1 7600 g. (c)		30°		a 12 93		1/n=0.485.	
P	V _a	V _t	X	X/M	log P	log X/M	X/M calc.
9 50	21 09	0 23	20 66	11 85	1 97772	1 01372	.. .
40 56	46 24	0 95	45 26	25 72	0 60810	1 41027	25 32
82 32	66 25	1 99	64 26	36 51	0 91551	1 56241	35 94
141 46	87 50	3.42	84 08	47 77	1 15063	1 67916	46 74
241 77	113 78	5 84	107 94	61 33	1 38340	1 78767	60 61
408 02	146 29	9 86	136 43	77 52	1 61068	1 88941	78 10
592 10	175 60	14 29	161 31	91 65	1 77240	1 96213	93 59
702 40	191 72	16 97	174 75	99 29	1 84650	1 99691	101 60

Expt XV.

2 1422 g. (c).		0°		a 29 14		1/n=0.43207.	
P	V _a	V _t	X	X/M	log P.	log X/M	1/n.
17 67	80 58	0 44	80 14	37 41	0 24724	1 57299	0.4387
34 92	109 40	0 87	108 53	50 66	0 54307	1 70457	0 4422
59 32	137 74	1 48	136 26	63 61	0 77320	1 80353	0.4384
88 16	161 65	2 21	159 44	74 43	0 94527	1 87175	0.4307
129 25	190 26	3 23	187.03	87.31	1 11143	1.94106	0.4287
179.46	218 28	4 49	213 79	99 80	1.25396	1.99913	0.4263
225.21	242.18	5 64	236 54	110 42	1 35259	2.04305	0.4277
317.51	283 25	7 95	275 30	128 51	1 50175	2.10893	0.4291
408.48	321.18	10.23	310.95	145.15	1 61117	2.16182	0.4327
522.41	363.63	13 08	350.55	163.64	1.71801	2 21389	0.4361
652.13	397.64	16.33	381.31	178.00	1.81433	2.25042	0.4331



1 5440 g. (c)			Expt. XVI.		0°.	
P	V ₀	V ₁	X	X/M.	log P	log X/M.
8 40	39 08	0 22	25 86	25 57	1.92428	1.40773
36 50	78 98	0 94	78 04	50 54	0 56229	1.70364
61 54	98 15	1 59	96.56	62 54	0 78916	1 79616
80 47	111 19	2 08	109 11	70 66	0 90563	1 84917
106.11	125 35	2 74	122.61	79.41	1 02576	1.89988
145 39	143 59	3 76	139 83	90 56	1 16254	1 95694
187 02	160 58	4 84	155 74	100 86	1 27189	2 00372
258 17	186 42	6 68	179 74	116 41	1 41185	2 06599
341 23	214 29	8 83	205.46	133 06	1 53305	2 12405
422 16	240 04	10 92	229 12	148 39	1 62548	2 17138
569 86	280 79	14 75	266 04	172 30	1 75577	2 23629
639 09	297 98	16 54	281 44	182 27	1 80556	2 26071

2 2224 g (c)			Expt XXIV			1/n=0 4279	
P	V ₀	V ₁	X	X/M	log P	log X/M	1/n
10 43	70 19	0 26	69 93	31 47	0 01828	1 49790	1 2248
31 83	111 04	0 80	110 24	49 60	0 50285	1 69548	0 4374
67 47	152 69	1 70	150 99	67 94	0 82911	1.93213	0 4301
105 35	182 47	2 66	179 81	80 91	1 02263	1 90800	0 4248
147 05	210 16	3 71	206 45	92 89	1 16747	1 96797	0 4218
190 59	234 94	4 81	230 13	103 55	1 28010	2 01515	0.4215
245.57	265 34	6 20	259 14	116 60	1 39017	2 06670	0 4252
310 58	293 37	7 85	285 52	128 47	1 49217	2 10880	0 4244
366 57	318 20	9 23	308 97	139 03	1 56415	2 14311	0 4268
467 79	360 28	11 82	348 46	156 79	1 67005	2 19532	0 4310
585 96	401 09	14 80	386 29	173.82	1 76787	2 24010	0 4324
720.15	429.74	18 18	411 56	185 18	1 85742	2 26759	0 4264

1 4310 g. (c).			Expt XXVIII			1/n=0 3471°.	
		33 4°.		5 76 32°.			
6 00	88 07	0 11	87 96	61 47	1 77815	1.71866	0 4234
20 40	132.28	0 31	131 91	92 18	0 30963	1 96484	0 2657
41.07	180.24	0 76	179.48	125 42	0 61352	2 09844	0 3355
72 00	229 43	1 29	228 14	159 42	0 85733	2 20254	0 3735
113 38	270.82	2 04	268 78	187 82	1 05453	2 27375	0 3709
242 00	313.54	4 35	309 19	216 06	1 38382	2 33457	0 3266
243 00	364.94	4 37	360.57	251 97	1 38561	2 40138	...
243.01	455.54	4 37	451 17	351 28	1 38562	2 49869

* These constants were calculated from all points, hence the slope of the curve is slightly less than indicated from the majority of the observations.

1.6660 g. (c)			Expt. XXIX.			1/n=0 3794.	
		—34 4°.		72 33.			
4.22	88 89	0 07	88 82	53.31	1.52531	1.72681	0.3536
13.85	136 00	0.22	135 78	81 50	0.14145	1.91116	0.3665
29.02	180 70	0 47	180 23	108 18	0 46270	2.03415	0 3778
50.07	229.31	0.79	228.52	137.17	0.69958	1.13726	0.3973
73.45	272 07	1.18	270 89	162 60	0 86599	2.21112	0.4051
116.62	321 86	1.88	319 98	192.06	1.06677	2.28344	0.3975
205.59	347.35	3.32	344.03	206 50	1.31300	2.31492	0.3470
232.66	426 30	3.73	432 55	260.00	1.36672	2.41497

Expt. XXVI.

1.2876 g. (c).		—54°.		α 112.7°.		$1/n = 0.405^a$.	
P.	V_a .	V_l .	X.	X/M.	log P.	log X/M.	
0.40	40.17	0.00	40.17	31.19	2.60206	1.49402	
4.16	103.07	0.06	103.01	80.00	1.61909	1.90309	
9.85	142.41	0.16	142.25	110.47	1.99344	2.04324	
17.55	184.65	0.28	184.37	143.19	0.24728	2.15591	
27.50	220.53	0.44	220.09	170.93	0.43933	2.23282	
44.70	268.31	0.63	267.68	207.89	0.65031	2.31783	
89.00	313.50	1.44	312.06	242.36	0.94596	2.38435	
88.05	352.39	1.44	350.95	281.44	
88.35	396.39	1.44	394.95	307.85	

* Constant obtained by neglecting that point when saturation was nearly reached. For this reason $1/n$ is slightly larger than is the case in Expts. XXVIII and XXIX.

Expt. XXV.

1.6892 g. (c)		—80°.		α^b .		$1/n^a$.	
B.	V_a .	X/M.	log P	log X/M.		V_{18} .	
0.13	84.97	50.30	2.11394	1.70157		
0.58	166.92	98.82	2.76343	1.99484		
1.65	249.71	147.82	1.21748	2.16973		
3.05	307.17	181.84	1.48430	2.25969		
4.60	349.11	206.67	1.66276	2.31528		
8.30	388.23	229.83	1.91908	2.36138		
8.85	433.54	256.65	1.94694	2.40934		
8.80	470.90	278.77	1.94448	2.44526		
8.85	512.35	303.31	1.94694	2.48187		

* V_1 correction negligible; ^b not calculated as saturation pressure is less than 1 cm. and hence no comparable values would be obtained.

In order to make clear how each calculation was obtained from the actual results, and exact reproduction of Expt. XXIII, a typical example of all runs, is given below.

The table is almost self-explanatory. The meaning of the symbols being as follows:

B = barometer reading in mm.

Buret = readings of the gas buret in mm. obtained from the cathetometer settings.

V_1 = buret readings transformed into cc. by aid of the calibration curve.

V_2 = V_1 corrected to standard conditions, 0° and 760 mm.

V_0 = difference between the V_1 readings, or, the total volume of gas introduced in cc. and under standard conditions.

V_l = volume of gas in the vapor phase above the gel. in cc. and under standard conditions.

* $X = V_0 - V_l$ total volume of gas adsorbed in cc.

M = weight of the gel. in g.

X/M = volume (cc.) adsorbed per g. of gel.

Time—In this column is given the time of introduction of the gas and also when pressure readings were made.

$p_1 - p_2$ = uncorrected pressure of the system in mm. of mercury.

P = pressure of system in mm. of mercury corrected to 0° and for capillary depression

D = density of the gel.

T = temperature of the constant temperature bath.

T_1 = temperature of adsorption bulb. At $+30^\circ$ and $+40^\circ$ $T = T_1$.

T_2 = weighted mean of adsorption bulb temperature and that of the remaining apparatus. In runs at $+30^\circ$ and $+40^\circ$ $T_2 = T_1 = T$.

V_2 = volume (cc.) of the adsorption bulb to point I (see Fig. 1). V_2 and V_1 were obtained by use of the following equations:

$$V_2 = \frac{V_2 \times B \times 273}{760 \times T} \text{ and } V_1 = \frac{(V_1 - M/D)P \times 273}{760 \times T_2}$$

Expt. XXIII.

Weight of bulb and gel	17.6478 g.	SO ₂	30°	Cap.	Depression =	7.0000 mm.					
Weight of bulb	15.8878 g.				D	= 2.1648					
Weight of gel (grams)	1.7600				Γ	= 21.08 cc.					
B.	Buret.	V ₂	V ₁	V ₀ .	V ₁	X	X/M.	Time	P ₁	P ₂	P ₁ -P ₂
766.10	182.30	97.02	88.12	21.09	0.23	20.86	11.85	12.15
765.30	312.80	73.88	67.03	1.00	201.70	185.34	16.36
.....	2.30	200.95	184.45	16.50
.....	3.15	200.65	184.10	16.55
765.30	312.80	73.88	67.03	25.15	0.98	45.26	25.72	3.15
765.00	471.20	46.18	41.88	46.24	4.00	252.90	205.15	47.75
.....	4.50	252.82	205.05	47.77
765.00	471.20	46.18	41.88	20.01	1.99	64.26	36.31	5.00
764.70	595.33	24.12	21.87	66.25	5.40	277.85	188.10	89.75
.....	8.00	278.25	188.60	89.75
764.70	595.33	24.12	21.87	21.25	3.42	84.08	47.77	8.10
764.95	726.88	0.68	0.62	87.50	8.30	339.90	190.70	149.20
.....	9.45	339.90	190.70	149.20
766.00	177.30	97.90	88.90	26.28	5.84	107.94	61.33	9.45
766.00	342.00	68.96	62.62	113.78	10.45	439.75	190.95	248.80
.....	11.30	439.70	189.90	249.80
.....	12.30	439.10	189.07	250.03
.....	1.00	438.95	188.92	250.03
766.00	342.00	68.96	62.62	32.51	9.86	136.43	77.52	1.10
765.00	544.65	33.20	30.11	146.29	3.15	622.50	205.40	417.10
.....	4.00	622.20	205.05	417.15
765.00	544.65	33.20	30.11	29.31	14.29	161.31	91.65	4.05
763.85	725.75	0.88	0.80	175.60	5.05	785.72	181.95	603.77
.....	5.50	785.60	181.70	603.90
.....	8.15	785.60	183.50	602.10
.....	8.45	785.80	184.00	601.80
763.85	180.20	97.38	88.18	16.12	16.97	174.75	99.29	9.00
763.15	281.00	79.65	72.06	191.72	16.97	9.45	887.40	176.80	710.60
.....	10.30	887.10	174.05	713.05
.....	11.00	887.10	174.05	713.05

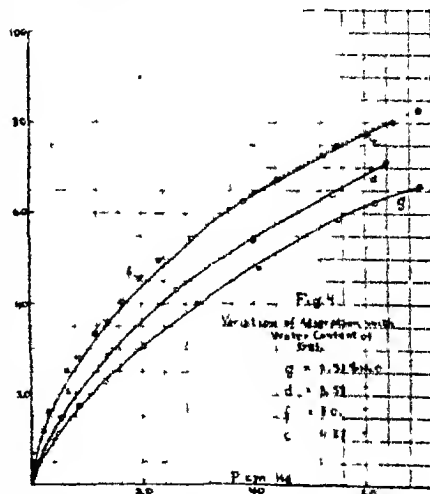
Water Content and Adsorption.

It was known from previous work¹ that, generally speaking, the adsorption of any gas was dependent upon the water content of the gel used. The fact that the gas or liquid was soluble or insoluble in water seemed

¹ Chemical Warfare Service paper, *loc. cit.*

to make no difference. It was also pointed out in this paper that a gel containing from 6 to 9% water seemed to be the most active. Such observations made it desirable to make measurements with gels of different water content.

As our method of treatment was static and its accuracy depended to a very great extent upon complete removal of all air before the run was started, we were limited to gels of very low water content, as lengthy evacuation and high temperatures were necessary to obtain air-free material. Gels with 2.31, 3.51, 4.86 and 9.97% water were used. The results are given below and are also shown graphically in Fig. 4. The sample containing 2.23% water is practically the lower limit, it being impossible to prepare a sample containing a smaller amount of water and at the same time preserve the structure of the gel. This fact may be used as an argument that a small amount of the water in the gel of silicic acid is not mechanically held, but is in some way intimately connected, chemically perhaps, with the silica network. A gel containing about 8% water was the upper limit, as with this amount at room temperature the gel has no vapor pressure and hence fairly good evacuation



without any appreciable loss of water could be accomplished. The curves speak for themselves, the isotherms with 9.97 and 4.86% lie practically on the same line, indicating that the maximum value of adsorption would be possessed by a gel containing an amount of water lying between these 2 values. This further confirms the statement made in the paper previously mentioned.

The fact that sulfur dioxide is very soluble in water suggests the idea of solubility, that is, increased water content should cause increased adsorption. This idea, although plausible, is contradictory to some of the observations, for it has been shown that there is a maximum water content above which adsorption decreases and does not increase. Furthermore, even in those cases where adsorption does increase with greater water content, the increase is entirely too large to be accounted for by solubility. For instance, the average difference in X/M for Samples g and d was 7 cc. The actual difference in the amount of water was

0.0120 g., which would adsorb at 40° about 0.5 cc. of sulfur dioxide, a value far too low for the difference actually observed.

It is believed that this difference in adsorption with small changes in water content might be due to the change caused in the size of the pores. If the water content is too low we have the pores too large and hence the capillary forces acting are enormously diminished and cause low values for adsorption. On the other hand, if the water content is too high we have the smaller capillaries partially filled and hence the space available for the gas is decreased. An adjustment of these 2 factors must be made to produce the best results.

Expt. XVII

2.4118 g. (g)		2.31% H ₂ O		40°	$a = 3.936$	$1/n = 0.678$	
P.	V ₀	V ₁	X	X/M	log X/M	log P	
14 60	10 93	0 34	10 59	4 39			
51 35	28 96	1 19	27 77	11 51	1 06108	0 71054	
90 53	44 28	2 09	42 19	17 49	1 24279	0 95679	
134 10	59 04	3 10	55 94	23 19	1 36530	1 12743	
204 85	79 35	4 73	74 62	30 94	1 49052	1 31143	
304 42	103 66	7 03	96 63	40 06	1 60271	1 48347	
409 16	125 37	9 45	115 92	48 06	1 68178	1 61189	
552 77	153 17	12 77	140 40	58 21	1 76507	1 74255	
626 57	165 65	14 47	151 18	62 68	1 79713	1 79696	
701 50	177 29	16 21	161 08	66 79	1 82471	1 84603	

Expt. X

1.8921 g. (d)		3.51% H ₂ O		40°	$a = 5.821$	$1/n = 0.600$	
P.	V ₀	V ₁	X	X/M	log P	log X/M	
45 76	27 68	1 06	26 62	14 07	1 65049	1 14829	
137 34	57 73	3 20	54 53	28 82	1 13780	1 45969	
263 77	87 62	6 14	81 48	43 06	1 42111	1 63407	
400 32	112 75	9 33	103 42	54 66	1 60241	1 73767	
549 71	134 41	12 81	121 60	64 37	1 74014	1 80868	
644 89	150 05	15 03	135 02	71 36	1 80946	1 85345	

Expt. XIV.

2.9980 g. (f)		8.01% H ₂ O		40°	$a = 8.129$	$1/n = 0.555$	
P.	V ₀	V ₁	X	X/M	log X/M	log P	
8 68	17 49	0 19	17 23	5 74			
25 25	37 02	0 57	36 45	12 16	1 08493	0 40226	
65 55	64 00	1 49	62 51	20 85	1 31911	0 81657	
88 20	85 61	2 00	83 61	27 89	1 44545	0 94547	
143 57	114 06	3 26	110 80	36 95	1 56761	1 15706	
232 02	154 21	5 27	148 94	49 68	1 69618	1 36551	
294 44	170 36	6 69	163 47	54 52	1 73656	1 46907	
388 54	196 24	8 83	187 41	62 51	1 79595	1 58943	
533 13	230 77	12 11	218.66	72 93	1 86291	1 72683	
651 00	254 91	14 79	240 12	80 09	1.90358	1 81358	

It was noticed that when the same charge was used for another run the amount adsorbed was distinctly less than in the original run. This

was due, without doubt, to the fact that it required more drastic treatment, longer evacuation and higher temperature, to remove the sulfur dioxide than it did in the case of the air originally present. During this process a small amount of water was removed and the result followed along the lines we have just discussed, decreased adsorption. In agreement with this conclusion is the further fact that where the gel originally started with was of low water content there was less difference between the first and second run. The following examples will show this more clearly. Compare Expt. XI with X, and Expt. IX with XVIII.

Expt XI

1.8921 g^a	30°			
P	V_0	V_1	λ	X/M
32 43	22 25	0 75	21 53	11 37
89 93	43 44	2 08	41 36	21.85
166 08	64 58	4 31	60 27	31 85
265 11	85 21	6 20	79 01	41 75
407 48	110 13	9 48	100 65	53 19
572 81	134 95	13 35	131 60	64 27
672 04	147 22	15 66	131 56	69 53

^a Previously used--originally (d) water content

Expt IX

2.1985 g^a	40°	$a = 8.727.$	$1/n = 0.5260$	
P	V_0	V_1	λ	X/M
20 90	27 64	0 50	27 14	12 34
74 20	57 44	1 72	55 72	25 38
152 00	85 68	3 55	82 13	37 31
335 48	130 87	7 79	123 08	55 98
574 74	173 34	11 33	160 01	72 78

^a Previously used--originally (c) water content.

Adsorption Reversible.

All earlier work on the adsorption of vapors by silicic acid gel showed a marked difference in the amount adsorbed at the same pressure and temperature, depending upon whether the pores were being filled or emptied. The earlier work of van Bemmelen¹ with water and later that of Anderson² with water, alcohol and benzene, all showed this wide difference in the filling and emptying process. They explained this hysteresis from the known fact that a liquid in a capillary tube has a greater vapor pressure when being filled than when being emptied, as in the former case we have a diminution of the curvature of the liquid meniscus due to incomplete wetting. This is a very plausible explanation as well as an interesting example of capillary phenomena. So it was thought desirable to obtain isotherms where the sulfur dioxide was removed from the gel instead of being added.

As has been stated above, this was accomplished by opening a carefully

¹ *Z. anorg. Chem.*, 15, 233 (1897); 18, 98 (1898).

² *Loc. cit*

evacuated soda-lime bulb to the system and when sufficient had been taken up removing the same and weighing. The weight was then changed to cc. at standard conditions by using the proper conversion factor.¹ All reversible measurements were made at 0°, as here we have a very large adsorption and the difference, if any, would for that reason be magnified. Expts. XXXII and XXXIII were the first reversible runs made.

Expt. XXXII.

1.1140 g. (c).		0°.		$\sigma = 32.95.$		$1/n = 0.4116.$	
Filling Pores.							
P.	V_0	V_1	X.	X/M.	log P	log X/M.	$1/n$
19.05	44.27	0.54	43.73	39.25	0.27989	1.59074	0.2716
52.10	78.16	1.18	76.98	69.10	0.71684	1.83048	0.4487
102.40	100.54	2.32	98.22	88.17	1.01030	1.94532	0.4231
188.40	127.13	4.28	122.85	110.28	1.27508	2.04250	0.4115
291.00	153.32	6.59	146.73	131.71	1.46389	2.11962	0.4111
453.50	189.12	10.27	178.85	160.10	1.65658	2.20439	0.4144
704.80	225.25	15.96	209.29	187.87	1.84807	2.27387	0.4091

Emptying Pores.

$\sigma = 37.13.$				$1/n = 0.38107.$		
P.	Wt. SO ₂	Vol. SO ₂	V ₀ .	V ₁	X	X/M
704.80	0.0000	0.00	225.25	15.96	209.29	187.87
445.76	0.1060	37.05	188.20	10.12	178.08	159.86
286.70	0.2060	72.00	153.25	6.30	146.75	131.73
149.96	0.3095	108.18	117.07	3.50	113.57	101.95
77.49	0.3828	133.79	91.46	2.21	89.25	80.12
19.00	0.4870	170.21	55.04	0.44	54.60	49.01
4.25	0.5459	190.80	34.45	0.10	34.35	30.85
P.	log P		X/M		1/n.	
704.80	1.84807		2.27387		0.3810	
445.76	1.64910		2.20374		0.3844	
286.70	1.45743		2.11969		0.3766	
149.96	1.17598		2.00838		0.3738	
77.49	0.88925		1.90374		0.3755	
19.00	0.27875		1.69028		0.4324	
4.25	1.62939		1.53593		

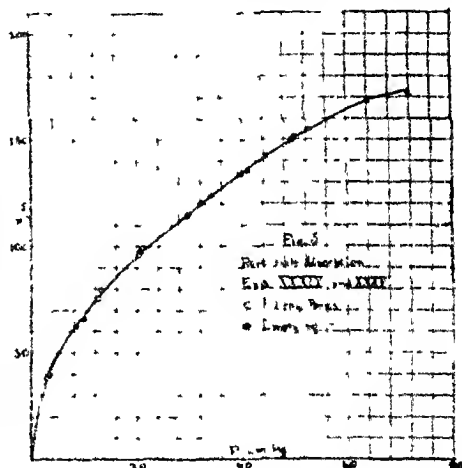
Expt. XXXIII.

2.6005 g. (c).		0°.		$\sigma = 29.222.$		$1/n = 0.4231.$	
Filling Pores.							
P	V ₀	V ₁	X.	X/M.	log P	log X/M.	1/n
12.11	84.17	0.27	83.90	31.67	0.08422	1.50065	0.4166
63.87	171.11	1.39	169.72	65.26	0.80530	1.81465	0.4334
115.00	216.11	2.55	213.56	82.12	1.06070	1.91445	0.4232
176.40	258.33	3.75	254.58	97.90	1.24650	1.99078	0.4212
265.07	307.42	5.77	301.65	116.00	1.42336	2.06446	0.4207
349.26	349.64	7.61	342.03	131.52	1.54315	2.11899	0.4234
453.00	396.16	9.87	386.29	148.54	1.65610	2.17185	0.4265
561.44	437.18	12.23	424.95	163.42	1.74930	2.21330	0.4268
745.95	474.81	16.23	458.58	176.35	1.87792	2.24637	0.4157

¹ Landolt-Börnstein, "Tabellen," gives one liter of sulfur dioxide at sea-level, 760 mm. and 0°, weighs 2.8611 g.

$a = 30.605$		Emptying Pores.			$1/n = 0.4119$.		
P	Wt. SO_2	Vol. SO_2	V_0	V_1	X	X/M	
745.95	...	0.00	474.81	16.23	458.58	176.35	
545.70	0.1062	33.12	437.69	11.85	425.84	163.75	
338.91	0.3614	126.32	348.49	7.38	341.11	131.17	
163.55	0.6386	223.20	251.61	3.56	248.05	95.39	
50.17	0.9106	318.27	156.54	1.09	155.45	59.78	
P	$\log P$		$\log X/M$	$1/n$		$(X/M)_F$	
745.95	1.87792		2.24637	0.4050			
545.70	1.73695		2.21418	0.4191		161.10	
338.91	1.53008		2.21783	0.4130		130.00	
163.55	1.21365		1.97950	0.4068		94.40	
50.17	0.70044		1.77656	0.3985		67.50	

In the last column, marked $(X/M)_F$, is given the amount adsorbed on filling for the same pressure values observed for the emptying process. In every case the former is the smaller value. Although this difference is small, nevertheless it is real. Doubt was at once raised whether all the air could be removed by the treatment used. If not, the first introduction of sulfur dioxide would liberate the air present and thus cause an increased pressure. On the first exposure to the soda-lime bulb practically all of the air would rush out and hence the pressure due to the air on the ascending curve would be eliminated and a greater adsorption at the same pressure would be observed. As a matter of fact, after the first exposure the MacLeod gage, used to indicate when all gas had been adsorbed, never showed a vacuum, but indicated the presence of 0.1-0.2 cc. of gas. This was not noticeable, or if so, very slightly after the first exposure.



It was now decided to prepare an absolutely air-free sample even at the expense of making a gel of only approximately known water content. This was accomplished by allowing the gel to stand in equilibrium with sulfur dioxide at about 70 cm. pressure overnight and then pumping it off and repeating the process. This was done 4 times and it is safe to say that the gel was completely freed from air. Two experiments were run with a sample thus prepared. The results are given on p. 964 and are shown graphically in Fig. 5.

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Expt. XXXIV.

2 3200 g ^a		0°.		c = 21 943		1/n = 0.4910.	
Filling Pores.							
P.	V ₀	V ₁	X	X/M	log P	log X/M	1/n
33 37	93 12	0.73	92 39	39 82	0 52336	1 60010	0 4944
131.14	182 60	2 87	179 73	79 27	1 11773	1 89911	0.4990
215 79	232 01	4 72	227 29	97 93	1 33403	1 99092	0 4869
305 14	276 46	6 68	269 78	116 28	1 48450	2 06551	0 4878
413 20	324 66	9 04	315 62	136 04	1 61616	2 13366	0 4902
529 44	369 68	11 58	358 10	154 35	1 72382	2 18851	0 4914
722.77	412 46	15 82	396 64	170 96	1 85900	2 23290	0 4790

Emptying Pores

a = 21 943.						1/n = 0.4910	
P	Wt SO ₂	Vol SO ₂	V ₀	V ₁	X	X/M	1/n
722 77			112 46	15 82	396 64	170 96	
498 27	0 1554	54 31	358 15	10 60	347 15	149 68	
341.10	0 3399	118 80	293 66	7 47	286 19	123 36	
209 71	0 5219	182 41	230 05	4 70	225 33	97 13	
85 25	0 7559	264 20	148 26	1 86	146 40	63 10	
P			log P			log X/M	1/n
722 77			1 85900			2 23290	0.4790
498 27			1 69747			2 17517	0 4913
341.10			1 53288			2 09118	0 4957
209.71			1 32162			1 98735	0 4858
95.25			0 93069			1 80003	0 4928

^a Sample (c) repeatedly evacuated

Expt. XXXV

2 3200 g ^a .		0°		a = 21.49		1/n = 0.4966		
Filling Pores								
P	V ₀	V ₁	X	X/M	log P	log X/M	1/n	X/M calc
31.61	90 11	0 67	89 44	38 55	0 49982	1 58602	0 5078	38.06
130 54	183 00	2 94	180 06	76 07	1 11574	1 88121	0 4913	75 21
205 28	227 85	4 35	223 50	96 34	1 31735	1 98381	0 4966	96 37
296.21	274 51	6 28	268 23	115 62	1 47160	2 06303	0 4965	115 62
397 70	320 47	8 43	312 04	134 51	1 59956	2 12879	0 4977	133 83
508 66	363 98	10 78	353 20	152 24	1 70643	2 16253	0 4983	151 23
648 57	405 53	14 19	391 34	168 67	1 81196	2 22704	0.4944	170.62

Emptying Pores

a = 21.943						1/n = 0.4910.	
P	Wt SO ₂	Vol SO ₂	V ₀	V ₁	X	X/M	1/n
648 57			405 53	14 19	391 34	168.67	
445.34	0 1878	65 64	339.89	9 43	330.46	142 44	
323 00	0 3381	118 17	287 36	6 63	280.73	121.00	
201.84	0 5128	179.21	226.30	4 27	222.03	95.70	
96 46	0 7118	248 70	157.74	2 04	155.70	67.11	
30 89	0 9058	316 59	88 94	0 65	88.29	38.06	

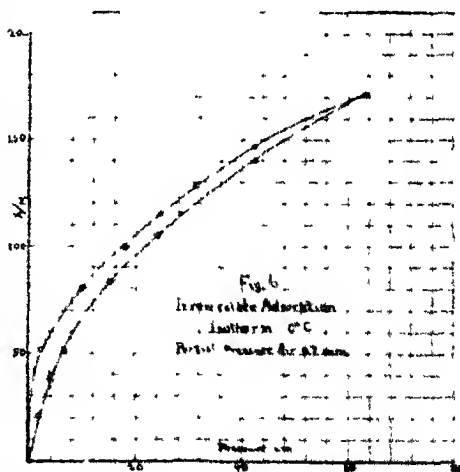
P	$\log P$	$\log X/M$	$1/n$	$(X/M)p$
648.57	1.8119	2.22704	0.4888
445.34	1.64869	2.15363	0.4926	143.00
323.00	1.50920	2.08279	0.4912	121.20
201.84	1.30501	1.98091	0.4901	95.80
96.46	0.98435	1.82679	0.4981	66.60
30.89	0.48982	1.58047	0.4881	37.80

* Charge of Experiment XXXIV evacuated

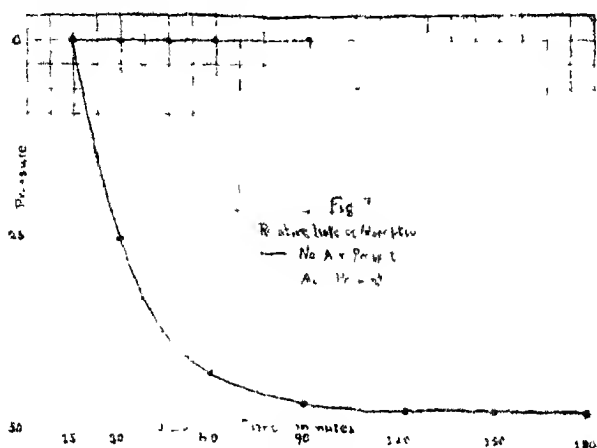
The agreement is well within the limit of experimental error. In other words, the adsorption of sulfur dioxide by silicic acid gel is a reversible process.

It will also be noticed that the absorption values do not agree with those previously made at this temperature. The reason for this may be found in the discussion given under the head of water content and adsorption. Here it was shown that by repeated exhaustion of the gel the water content of the gel is decreased and hence its adsorptive power (in this case) is at the same time lowered.

In order to prove more conclusively that minute traces of air were responsible for the lack of reversibility a sample was run where there was a definite amount of air present. This was done by evacuating the bulb but a short space of time. To be exact, there was at the beginning of the run a partial pressure of air of 0.7 mm. The experiment was carried out in exactly the same manner as previous reversible runs. The experimental facts are given in Table II and Expt. XXXVII. They are also shown graphically in Fig. 6. Table II is given to show the large effect of small amounts of air upon the rate of adsorption. With air present, as may be seen, it is a question of hours before equilibrium is reached, while under conditions of a perfect vacuum equilibrium is reached in a very few minutes. The fact that there is an appreciable time factor at all in the latter case is caused chiefly by the time necessary for the dissipation of the heat evolved during adsorption. In Fig. 7 are plotted the rates of adsorption in the form of dp/dt for two points, one obtained in the presence of air and the other in the absence of air. This gives another strong evidence of what important role air plays in adsorption



phenomena. The presence of this substance is suggested as a possible reason for the hysteresis observed by previous workers on reversible adsorption isotherms.



Expt XXXVII.*

2.7430 g. (c).

0°.

 $1/\pi = 0.4569$

Filling Pores.

P.	V_0	V_1	X	X/M	log P	log X/M
25.28	56.97	0.54	56.43	20.57	0.40278	1.31323
46.05	104.32	0.99	103.33	37.60	0.66323	1.57519
69.20	148.09	1.49	146.60	53.44	0.84011	1.72787
148.37	230.27	3.19	227.08	82.78	1.17135	1.91793
284.86	320.64	6.13	314.51	114.66	1.45463	2.05941
424.55	396.48	9.12	387.36	141.22	1.62793	2.14989
636.35	487.38	13.67	473.71	172.70	1.80369	2.23729

Emptying Pores.

 $1/\pi = 0.4012$.

P.	Wt. Sn.	Vol. Sol.	V_0	V_1	X	X/M
636.35	0.0000	0.00	487.38	13.67	473.71	172.70
425.50	0.2114	73.89	413.49	9.15	404.34	147.41
318.13	0.3711	129.71	357.67	6.68	350.99	127.96
181.71	0.5999	209.67	277.71	3.90	273.81	99.82
107.64	0.7571	264.62	223.76	2.31	221.45	80.73
27.66	0.9818	343.15	144.23	0.58	143.65	52.37
P.	log P.			log X/M		(X/M) _P
636.35		1.80369		2.23729	
425.50		1.62890		2.16853		141.50
318.13		1.50264		2.10707		122.00
181.71		1.25937		1.99922		92.50
107.64		1.02197		1.90703		72.00
27.66		0.44185		1.71908		25.00

* Partial pressure of air at beginning of experiment of 0.7 mm. of Hg.

TABLE II.		
<i>X/M.</i>	Time (min)	Pressure (mm)
20 57	40	30.60
	115	26.40
	145	25.80
	185	25.30
	215	25.30
37 60	40	51.50
	70	47.70
	100	46.75
	130	46.25
	205	46.20
53 44	15	93.90
	45	75.95
	75	71.00
	105	69.80
	135	69.65
	165	69.40
82 78.	195	69.45
	15	195.99
	30	170.50
	60	153.10
	90	149.35
	125	148.70
114 66	150	148.85
	180	148.85
	15	343.65
	45	308.20
	75	291.05
141.22.....	250	285.75
	280	285.80
	15	500.10
	30	461.40
172.70.....	125	428.40
	155	425.00
	185	426.05
	215	425.95
	255	425.95
Total time.....		25 hours, 45 minutes.

Discussion.

Certainly there must be a mathematical interpretation possible and from the well defined regularity and similarity of the curves this appears to be far from complicated. A brief review of those equations in general use is certainly appropriate.

Many adsorption formulas have been proposed. That of Arrhenius,¹ later amplified by Schmidt,² is certainly logical and has been used over a wide range of cases. It has the following form when applied to gases:

$$pS = ke^{A(S-x)/S}$$

where p is the pressure of the gas, S the amount adsorbed at saturation per gram of substance, x the amount adsorbed at the different pressure intervals, K and A are constants and e has its usual value. Changing this somewhat, we may write

$$x = \frac{pS}{Ke^{A(S-x)/S}},$$

which states that the amount adsorbed is equal to the product of the pressure, the saturation value and a constant, itself a function of the temperature, which fact is expressed by the power $\frac{A(S-x)}{S}$ to which e is raised. Written in the logarithmic form,

$$\log p - \log S = \log K - \log x - \frac{A(S-x)}{S} \log e,$$

since $\log e$, A and S are constants, and, as Schmidt has shown, $\log K = k - \log S$, the expression is simplified, giving

$$\log p - \log x - B(S-x) = k.$$

This gives an equation well suited for calculation purposes. The results of adsorption of sulfur dioxide by silica gel fits excellently this equation when the isotherms at the higher temperatures are used, those above 0° . Even those at the lower temperatures give fairly satisfactory results if proper manipulation of the constant B is made. The value of k increases with the temperature while there is a tendency for B to remain constant, although this also seems to increase with temperature. Theoretically B should remain unchanged throughout the temperature range.

A great drawback to this equation, as has been pointed out before by Marc,³ is that it is too pliable. For instance, fixing arbitrarily the value of S the constant B may vary through wide limits and still fit the observations. Also, the value S can be changed at will and by slight changes in B and k the observations are again correlated. Another objection is the fact that S is not a constant through a wide temperature range. It is logical to believe that it must vary with the density of the condensed gas. This correction would be considerable and would give another variable to contend with in the Schmidt equation.

The adsorption ideas of Langmuir⁴ in their present form are not applica-

¹ S. Arrhenius, *Medd. K. Vetenskapskad. Nobelinst.*, 2, 7 (1911).

² G. C. Schmidt, *Z. Phys. Chem.*, 78, 667 (1912).

³ Marc, *ibid.*, 81, 679 (1913).

⁴ *THIS JOURNAL*, 39, 1848 (1917); 40, 1361 (1918).

ble to the measurements of adsorption by porous bodies. The stray field of force, emanating from the surface of the adsorbent, it is believed, reaches out, attracts and holds those molecules of the gas that approach its surface. The maximum adsorption is reached when this surface is covered by a film of the adsorbed substance which is but a molecule in thickness. Hence, from this theory, other factors being equal, adsorption is dependent primarily upon the amount of surface exposed. The fact that the pressure of the gas phase changes gradually is ascribed to the difference in the strength of the individual lines of force given off from the surface. Much evidence is brought forth to support this conception. Thus, in order to apply the formula to porous bodies a measure of the internal surface would be necessary. The difficulty of such an undertaking is easily seen. It is true that a rough approximation might be arrived at by making ultramicroscopic measurements of the size of the pores, such as Zsigmondy¹ has done in the case of silicic acid gel, and combining this value with that number representing the internal volume of a definite mass of the substance. This, at least, would give an idea of the internal surface. Yet, granting that a fairly accurate estimation were possible, it certainly must be admitted that forces other than residual valence come into play, especially so when the pores themselves approach the vicinity of molecular dimensions. This fact Langmuir recognizes and suggests that true adsorption should deal with plane or smooth surfaces only. It is thus evident that the observations made in this investigation cannot be expressed by the Langmuir equation in its present form.

The simplest and most widely used adsorption equation is that proposed by Freundlich. This is purely an empirical relation, but one that is very elastic and easy of manipulation. If x is the amount adsorbed, m the mass of the gel, p the pressure of the gas, a and $1/n$ constants, the equation is expressed as follows:

$$x/m = ap^{1/n},$$

or writing in the logarithmic form,

$$\log x/m = \log a + 1/n \log p.$$

This is an equation of a straight line and hence the constants a and $1/n$ are easily interpreted— a being the amount adsorbed when the pressure is unity, and $1/n$ representing the slope of the line. It is readily seen that the constants change with a change from one temperature to another. So in order to make a perfect general equation this change must be expressed.

An inspection of Figs. 2 and 3 will show that the results obtained with silica gel and sulfur dioxide are very well represented by the Freundlich equation. For this reason the constants a and $1/n$ have been given in

¹ *Loc. cit.*

the tables containing the data. The value of $1/n$ given at the head of each experiment was obtained by the method of mean errors and from that the value of a was found by substitution in one of the equations. This value of a , you will notice, corresponds very closely to what would be read from the graph shown in Fig. 3.

A very exhaustive treatment of this equation and its relation to temperature is given by Freundlich¹ and for this reason it is not necessary to carry through the somewhat extended proof for the validity of the general equation, which takes into consideration all the variables—pressure, temperature and amount adsorbed. It has the following form.

$$\log (x/m)_t = \log (x/m)_0 - (z - y \log p)t,$$

where $z = -\frac{d \log a}{dt}$ and $y = \frac{d 1/n}{dt}$. These values y and z should be constants and although the experimental results do not strictly bear this out, yet there is sufficient constancy to make calculations that give good approximate agreement. Table III gives the observed values and those calculated from the equation above, using the observations made in Expts. XVIII and XIX. For this particular sample of gel $z = -0.0146$ and $y = 0.0035$, values obtained by taking a weighted mean of these differentials actually observed at the temperatures from 0° to 100° .

TABLE III.

Expt. XVIII (c) 40° .			Expt. XIX (c) 80°		
P	X/M obs	X/M calc	P	X/M obs	X/M calc
9 44	7 50	. .	47 00	4 48	6 20
31 37	16 50	14 45	192 19	16 73	16 75
64 77	25 25	22 62	224 73	18 66	18 70
110 00	33 66	30 73	407 88	27 70	28 99
169.13	41 88	39 01	575 32	34 17	37 05
299.78	53 54	53 91	671 95	37 41	41 20
448 60	67 17	67 99			
567 52	75 07	77 31			
692 20	82 16	84 36			

The objectionable feature of the Freundlich equation, as well as to most all other adsorption formulas yet proposed, is that isotherms at many different temperatures have to be made in order to obtain the proper value of the constants to be used for adsorption values at any pressure and at any temperature. There is no way of predicting or even roughly approximating what the adsorption would be at a temperature, say 40° , knowing the adsorption at some other temperature, say 0° . This means that a very large number of experiments must be made on every system before it can be properly disposed of and cataloged. This point will be taken up more fully in the latter part of the paper.

The accuracy of the measurements and the ease with which they can

¹ Freundlich, "Kapillarchemie," p. 101.

be reproduced is clearly shown by Expts. XV, XVI and XVII, which were carried out on different dates with 2.1422 g., 1.5440 g. and 2.224 g. of gel, respectively. The values of X/M at equal pressures were calculated by the aid of the Freundlich equation. These calculations are found in Table IV.

TABLE IV
 X/M Calculated from $1/n$ and a Values

P (Cm)	Expt XV June 26	Expt XVI July 4	Expt XXIV Sept 16
5	58.45	56.70	59.36
10	78.68	77.33	79.86
15	93.63	92.73	94.97
20	105.91	105.48	107.40
25	113.90	116.55	118.16
30	126.03	126.47	127.75
35	134.64	135.51	139.64
40	142.58	143.86	144.48
45	149.93	151.66	151.95
50	159.58	158.98	158.96
55	161.44	165.91	165.57
65	175.57	178.80	177.84

In Fig. 3 we have plotted $\log X/M$ against $\log p$. If the equation held absolutely we would have a system of straight nearly parallel lines. This is not strictly true. There are deviations in both directions, but more noticeably so with those isotherms carried out at the extreme temperatures. This bending is concave towards the x -axis, and for high temperatures takes place at the extreme left, while at the lower temperatures it occurs at the extreme right. The first case is probably due to the slight pressure developed by the adsorbed air released on the introduction of the first amount of sulfur dioxide. This pressure, although extremely small in itself, is, in proportion to the pressure of sulfur dioxide relatively large at this part of the curve and hence would produce a noticeable effect. More will be said later in regard to this point. The bending in the case of the lower temperatures is easily accounted for. In that region the vapor pressure of the liquid is approached and deviations would not be surprising but expected. Others¹ have shown that where p/p_0 approaches unity the Freundlich equation is not applicable.

The mere fact that a chemically inert substance like silica gel is found exhibiting such marked adsorptive properties is sufficient in itself to indicate that the cause of adsorption does not lie in the interaction of adsorbent and adsorbed substance. In making the above statement we do not mean to say that it covers all the cases of gas or vapor adsorption, for the fact of specific gas adsorbents would tend to disprove it, *e. g.*, palladium for hydrogen. Perhaps it would be better to confine ourselves to the ad-

¹ Titoff, *Z. physik. Chem.*, 74, 641 (1910); L. B. Richardson, *THIS JOURNAL*, 39, 1828 (1917).

sorption of vapors, although it will be seen that our analysis permits the extensions to regions that are ordinarily considered as gaseous. As an approximate line of division we might select the critical temperature and confine ourselves to a discussion of adsorption occurring below this temperature. It cannot be too strongly emphasized that we are dealing with phenomena that exhibit adsorption to a marked degree, and are not manifestations of layers of a few molecules deep.

It is our belief that the adsorption of gases or vapors, let us say at all temperatures below the critical temperature, may be predicted from a knowledge of the physical constants of the gas or vapor alone. Furthermore, the role of the adsorbent is simply that of a porous body, its chemical nature being a matter of indifference. (Cases of obvious chemical affinity are of course excluded.) Adsorbents differ in the extent of their total internal volume and also in the dimensions of the spaces, called pores for simplicity, that make up the internal volume. It is conceivable that 2 adsorbents may possess the same internal volume but show marked differences in the adsorption of the same vapor due to differences in the distribution of the pore sizes.

If this is true the form of the adsorption curve expresses the distribution of the internal volume as a function of the dimensions of the pores. An attempt was made to express this relation in terms of the Maxwell distribution law, but a moment's reflection will convince one that there is no reason to expect the pore sizes to be distributed according to the laws of probability. The pores in the silica gel exist as the result of the juxtaposition of colloidal particles which are approximately all of equal dimensions and are, therefore, probably V-shape in cross section, or at any rate may be designated as tapering.

It is at once evident that if the adsorption curve simply shows the manner in which the various sized pores are distributed that go to make up the internal volume of the adsorbent, then, instead of seeking a relation between weight of adsorbed gas and the equilibrium pressure we should at once turn to the volume occupied by the adsorbed gas. As a matter of fact, if we express our isotherms of sulfur dioxide adsorption with volume of liquid sulfur dioxide as ordinates instead of weight, the curves are brought closer together. Our next consideration is, of course, to express the abscissas of our isotherms not as simple equilibrium pressures but as corresponding condensation pressures.

It has long been known that the properties which determine the ease of condensation of a gas or vapor are closely connected with the physical constants of the gas or vapor which are of importance in determining the magnitude of the adsorption. It is well known that condensations of vapors occur with greater ease in capillary tubes than on a level surface, provided the liquid wets the capillary wall. This phenomenon

has been long studied and the lowering of the vapor pressure of a liquid in a capillary in terms of the ordinary vapor pressure of the liquid P_0 is given by the following relation:

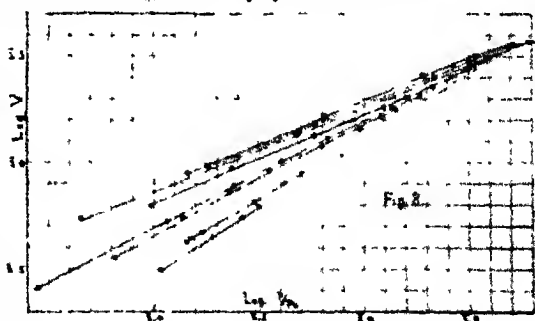
$$\ln P = \ln P_0 - \frac{2\sigma d}{DP_0 r},$$

where σ is the surface tension, d the density of the saturated vapor, D the density of the liquid and r the radius of the capillary. With the aid of this relationship we can readily derive the fact that the radius of the tube must be very small in order to have an appreciable effect on the vapor pressure of the liquid inside. It is not until we get to tubes of less than 0.001 mm. in diameter that we begin to affect the vapor pressure. From this it is clear that if we wish to account for the marked lowering of the vapor pressure in the case of adsorption, pores approaching molecular magnitude must be assumed. It is our feeling that such a wide extrapolation of the above formula is not justified and in the present analysis we shall not consider the question of absolute diameter of pores.

If we wish to compare the adsorption of a particular adsorbent for a gas or vapor at various temperatures, it is evident that the comparison must not be made at the same pressure, but rather at some corresponding pressure. As suggested by Williams and Donnan¹ the value of p/p_0 may be selected for this purpose (p_0 is the vapor pressure of the condensed vapor).

In Fig. 8 we have plotted the logarithms of the volumes of condensed sulfur dioxide (obtained by dividing the weight of sulfur dioxide by the density of liquid sulfur dioxide at the corresponding temperature) as ordinates against the values of logarithm p/p_0 as abscissas. It will

be noted that greater volumes are taken up at lower temperatures at the same corresponding pressures. Furthermore, it is to be noted that all the adsorption isotherms are brought much closer together. When p/p_0 equals unity the

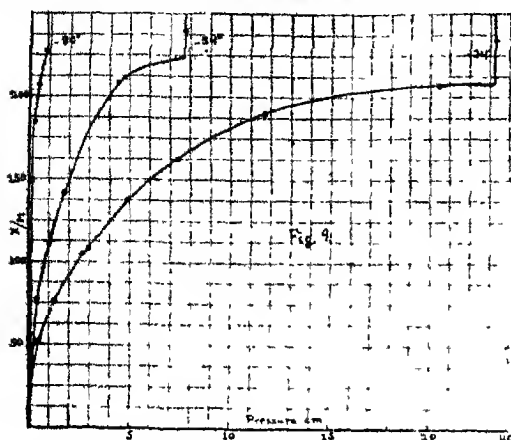


same volume of sulfur dioxide is taken up at all temperatures. At the higher temperature we were unable to work with pressures sufficiently great to enable us to realize the value of unity for p/p_0 , however, the slope of the log curves is such as to bring all curves together at the point $p/p_0 = 1$.

An approximate idea of exactly what this volume is may be grasped by

¹ Williams and Donnan, *Trans. Faraday Soc.*, 10 (1914).

reference to Fig. 9. Here are plotted on a larger scale the results obtained at the lower temperatures, in fact those temperatures where the



saturation point was reached. This point is easily fixed by the very sharp break in the curve. Introducing density correction, these values become almost identical. Table V gives these results, corrected and uncorrected, as well as the saturation value of the isotherm at 0° calculated from the adsorption equation. The accuracy

of the Freundlich equation does not permit calculation of the saturation points at the higher temperatures as a wide deviation would be expected.

TABLE V.

Temperature.....	-80°	-54°	-34°	0°
Vol. gas phase, cc.....	232	228	216	209
Vol. liquid phase, cc. (or internal vol. of gel)	0.4073	0.4168	0.4039	0.4167

Similar results with silica gel were obtained by Bachmann.¹ This investigator showed that with the same sample of gel at the saturation pressure, that is the vapor pressure of the liquid at that temperature, the same volume of different liquids was taken up. Some experiments were carried out in which the liquid was introduced through the gas phase; others where the gel was introduced directly into the liquid. In this latter case the surface was carefully wiped with filter paper and possible errors from this source minimized. The author states that no correction for contraction or other volume change resulting from possible forces acting within the gel structure was considered in the calculation. A few determinations are given.²

18°.	Sample 2.	0.3572 g. gel.
Liquid.	Wt. absorbed	Vol. per g. of gel.
	G	Cc.
H ₂ O.....	0.2276	0.6210
C ₆ H ₆	0.8791	0.6270
C ₂ H ₅ Br.....	0.6720	0.6210

¹ W. Bachmann, *Z. anorg. Chem.*, 79, 202 (1913).

² Other gel samples gave consistent although different values from the above.
e. g., Sample 5—vol. = 0.3621 cc.; loc. cit.

The absolute value is not in agreement with that found in this investigation, but it must be remembered that the experimental method as well as the gel sample itself was different. The main point is that with the same gel sample there is an equal volume of the liquid adsorbed, no matter what the liquid or what the temperature.

Up to this point we have considered the lowering of the vapor pressure from the simple standpoint as being due to the rise in a capillary tube. Clearly, in our case the effect is not due to a difference in level, nor is it certain that we are dealing with tubes opened at both ends. For our purpose it is better to consider the lowering of the vapor pressure of the liquid in a pore as due to a negative tension exerted on the liquid around the meniscus. Thus this pull has its origin in the tendency of films which wet the walls to contract so as to expose as little of surface as possible. Looking at the adsorption of vapors in this light, it is seen that the condensed vapor is under a tension rather than a pressure. Furthermore, it is a simple matter to calculate the magnitude of this negative pressure. Using the well-known Gibbs relation,

$$\left(\frac{dp}{dP}\right)_T = \frac{V}{v},$$

where dp = change in the vapor pressure, dP = change in the hydrostatic pressure, V = volume of the condensed phase, and v = volume of the gas phase, expressing the variation of vapor pressure with the hydrostatic pressure, we can calculate that liquid sulfur dioxide at 30° , having a vapor pressure of 3496 mm when in a capillary tube under a vapor pressure of 955 mm. is subject to a tension of about 530 atmospheres. When the pressure over the condensed liquid sulfur dioxide has risen to 706 mm. by the above relationship it can be shown that the negative pressure has fallen to 420 atmospheres. It is evident that we are in a position to calculate the negative pressure on any liquid provided we know the lowering of the vapor pressure, and the density of the condensed phase. (It is assumed that the vapor obeys the gas laws.)

If the liquid is in a closed tube this pull must occasion a dilation of the same to an extent that is proportional to the compressibility of the liquid. Worthington¹ has stated that the volume changes caused by negative pressure may be calculated with the aid of the compressibility coefficient. Unfortunately, we have no direct measurements of the compressibility of liquid sulfur dioxide and are, therefore, unable to evaluate quantitatively the volume change. It is known that in some cases² the relation

$$\beta\sigma^{1/2} = K$$

¹ Worthington, *Trans. Roy. Soc. (London)*, 183A, 355 (1892)

² Richards, *This Journal*, 40, 59 (1919)

holds good, but it has only been tested over a narrow range of σ and many exceptions have been noted. We can, however, say that liquids of high surface tension have smaller compressibilities than liquids of low surface tension

Here we have a possible explanation for the fact that the volume of sulfur dioxide at corresponding pressures are smaller at high than at low temperature. At the higher temperature the condensed phase is more compressible, σ , being smaller, and in addition the negative pressure is greater. In other words, we do not know the actual density of the condensed phase in the gel, but in all cases it is lower than the normal density which it approaches when $p/p_c = 1$.

Expt XII 100°			Expt XXIII 30°		
$\sigma = 9.25$, $D = 1.111$, $p_0 = 2114.3$ cm			$\sigma = 22.75$, $D = 1.3556$, $p_0 = 349.6$ cm		
log V.	log p/p_0	log $p\sigma/p_0$	log V	log p/p_0	log $p\sigma/p_0$
$\bar{2}$ 49183	$\bar{2}$ 03643	$\bar{1}$ 00257	$\bar{2}$ 39811	$\bar{3}$ 33415	$\bar{2}$ 69113
$\bar{2}$ 66113	$\bar{2}$ 27363	$\bar{1}$ 23977	$\bar{2}$ 73466	$\bar{2}$ 06453	$\bar{1}$ 42151
$\bar{2}$ 75343	$\bar{2}$ 41060	$\bar{1}$ 37674	$\bar{1}$ 88680	$\bar{2}$ 37194	$\bar{1}$ 72892
$\bar{2}$ 80302	$\bar{2}$ 50189	$\bar{1}$ 46803	$\bar{1}$ 00355	$\bar{2}$ 60706	$\bar{1}$ 96404
			$\bar{1}$ 11206	$\bar{2}$ 83981	$\bar{0}$ 09681
			$\bar{1}$ 21360	$\bar{1}$ 06711	$\bar{0}$ 35698
			$\bar{1}$ 28652	$\bar{1}$ 22881	$\bar{0}$ 58581
			$\bar{1}$ 32130	$\bar{1}$ 30301	$\bar{0}$ 65999

Expt XVIII 40°			Expt XIX 80°		
$\sigma = 21.0$, $D = 1.3111$, $p_0 = 471.2$ cm			$\sigma = 13.1$, $D = 1.192$, $p_0 = 1368$ cm		
log V	log p/p_0	log $p\sigma/p_0$	log V	log p/p_0	log $p\sigma/p_0$
$\bar{2}$ 21395	$\bar{3}$ 30176	$\bar{2}$ 62398	$\bar{2}$ 60374	$\bar{2}$ 14764	$\bar{1}$ 26491
$\bar{2}$ 55637	$\bar{3}$ 82330	$\bar{1}$ 14552	$\bar{2}$ 64115	$\bar{2}$ 21557	$\bar{1}$ 33284
$\bar{2}$ 74115	$\bar{2}$ 13816	$\bar{1}$ 46038	$\bar{2}$ 82272	$\bar{2}$ 47444	$\bar{1}$ 59171
$\bar{2}$ 86600	$\bar{2}$ 36818	$\bar{1}$ 69040	$\bar{2}$ 91388	$\bar{2}$ 62382	$\bar{1}$ 74109
$\bar{2}$ 96090	$\bar{2}$ 55501	$\bar{1}$ 87723	$\bar{2}$ 95323	$\bar{2}$ 69124	$\bar{1}$ 80831
$\bar{1}$ 08350	$\bar{1}$ 80359	$\bar{0}$ 12581			
$\bar{1}$ 16607	$\bar{1}$ 97865	$\bar{0}$ 30087			
$\bar{1}$ 21436	$\bar{1}$ 08077	$\bar{0}$ 40299			
$\bar{1}$ 25355	$\bar{1}$ 16702	$\bar{0}$ 48944			

Expt XXVI -54°			Expt XXV. -80°		
$\sigma = 39.0$, $D = 1.565$, $p_0 = 88.3$ mm			$D = 1.6295$, $\sigma = 44.5$, $p_0 = 8.8$ mm.		
log V	log p/p_0	log $p\sigma/p_0$	log V	log p/p_0	log $p\sigma/p_0$
$\bar{2}$ 75603	$\bar{3}$ 65610	$\bar{1}$ 24716	$\bar{1}$ 94694	$\bar{2}$ 16946	$\bar{1}$ 81782
$\bar{1}$ 16510	$\bar{2}$ 67313	$\bar{0}$ 26419	$\bar{1}$ 23931	$\bar{2}$ 81895	$\bar{0}$ 46731
$\bar{1}$ 30525	$\bar{1}$ 04748	$\bar{0}$ 63854	$\bar{1}$ 41420	$\bar{1}$ 27300	$\bar{0}$ 92136
$\bar{1}$ 41792	$\bar{1}$ 29832	$\bar{0}$ 88938	$\bar{1}$ 50416	$\bar{1}$ 53982	$\bar{1}$ 18818
$\bar{1}$ 49483	$\bar{1}$ 49337	$\bar{1}$ 08443	$\bar{1}$ 55975	$\bar{1}$ 71728	$\bar{1}$ 36564
$\bar{1}$ 57984	$\bar{1}$ 70435	$\bar{1}$ 29141	$\bar{1}$ 60585	$\bar{1}$ 97460	$\bar{1}$ 62296

Expt. XXIX.

-34.4°

$\sigma = 36.2$, $D = 1.5302$, $p^\circ = 232.6$ mm. $\sigma = 28.5$, $D = 1.435$, $p^\circ = 116.2$ cm.

$\log V$	$\log p/p_0$	$\log p\sigma/p_0$
$\bar{2}.99858$	$\bar{2}.25870$	$\bar{1}.81741$
$\bar{1}.18293$	$\bar{2}.77484$	0.33355
$\bar{1}.30592$	$\bar{1}.09609$	0.65480
$\bar{1}.40903$	$\bar{1}.33297$	0.89168
$\bar{1}.48280$	$\bar{1}.49938$	1.04809
$\bar{1}.55521$	$\bar{1}.70016$	1.25887
$\bar{1}.58669$	$\bar{1}.94639$	1.50510

Expt. XXIV.

0°

$\log V$	$\log p/p_0$	$\log p\sigma/p_0$
$\bar{2}.79757$	$\bar{3}.95307$	$\bar{1}.40755$
$\bar{2}.99515$	$\bar{2}.44763$	$\bar{1}.90211$
$\bar{1}.13180$	$\bar{2}.76370$	0.21818
$\bar{1}.20767$	$\bar{2}.95742$	0.41190
$\bar{1}.25764$	$\bar{1}.10226$	0.55674
$\bar{1}.31482$	$\bar{1}.21489$	0.66937
1.36637	$\bar{1}.32496$	0.77944
1.40847	$\bar{1}.42696$	0.88244
$\bar{1}.44278$	$\bar{1}.49994$	0.95442
1.49499	$\bar{1}.60484$	1.05932
$\bar{1}.53977$	1.70266	1.15714
$\bar{1}.56726$	$\bar{1}.79221$	1.24669

As an empirical relationship, the result of dividing the volume of the condensed sulfur dioxide by the value of the surface tension raised to a fractional power was tried. Qualitatively, this produces a correction in the right direction. In order to take into consideration the constant that connects the value of the surface tension with the change of volume, we have thrown our relation into the following form.

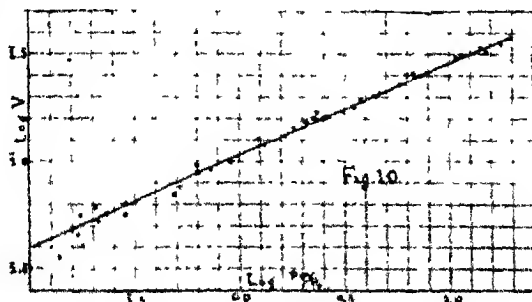
$$\frac{V}{\sigma^{1/n}} = k(P/P_0)^{1/n}$$

which, for calculation purposes, can be arranged thus

$$V = K \left(\frac{P\sigma}{P_0} \right)^{1/n}$$

assuming that the same value of $1/n$ holds both for p/p_0 and σ .

The preceding tables show the value of V , p/p_0 and $P\sigma/p_0$, all expressed as logs for convenience in plotting. Fig. 10 shows the contents of these tables when plotted with $\log V$ as abscissas and \log of $P\sigma/p_0$ as ordinates.



From this logarithm curve the value of the constant $1/n$ and k are found to be 0.447 and 0.1038. In this case k has been taken as that

volume where $\frac{P\sigma}{p_0} = 1$ and $1/n$ has its usual significance—the slope of the curve. Hence our adsorption equation for the system silica gel—sulfur dioxide would be,

$$V = 0.1038 \left(\frac{P\sigma}{p_0} \right)^{0.447}.$$

where V is expressed in cubic centimeters, σ in dynes/cm., and p and p_0 in the same unit of pressure. The close agreement is very striking and is strong evidence of our claim that the volume occupied by the adsorbed vapor is the same at the same value of the corresponding pressure p/p_0 .

Summary.

1. The adsorption of sulfur dioxide by silica gel was measured at various temperatures between -80° and $+100^\circ$.
2. The effect of the water content of the silica gel was studied. Maximum adsorption was shown by gels containing about 7% water.
3. The adsorption was shown to be reversible in the absence of air. In the presence of small amounts of air the rate of adsorption was greatly decreased and adsorption and desorption were irreversible.
4. The empirical equation of Freundlich was found to hold over almost the entire range studied—exceptions being at these points where the saturation pressure was approached.
5. The equation

$$\frac{V}{\sigma^{1/n}} = K(p/p_0)^{1/n},$$

is found to hold, where V = volume of condensed phase uncorrected, σ the surface tension, p the pressure of the gas phase, p_0 the vapor pressure of the liquid, k and $1/n$ constants dependent upon the physical properties of the adsorbent.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

A SURFACE CONDENSATION ERROR IN CERTAIN MEASUREMENTS OF VAPOR PRESSURE BY THE GAS CURRENT SATURATION METHOD.

BY ALAN W. C. MENZIES.

Received March 20, 1920.

In the employment of the method referred to in the title, the possibility of condensation of the saturated vapor on surfaces earlier in the apparatus train than the weighed absorption tubes has been appreciated by some investigators but neglected by others. In order that the seriousness of this source of error in the case of water may be more fully understood, the writer proposes to illustrate its incidence in certain investigations

and to report the results of experiments that give an idea of the magnitude of the error in the case of glass and of asbestos surfaces.

Saturated Water Vapor and the Gas Laws.—It may be well to clear the ground by stating that the assumptions that even the saturated vapor of water in air at ordinary temperatures and pressures is of normal density as computed from a molecular weight of 18.016 and a standard gram molecular volume of 22.40 liters by the gas laws, and that Dalton's law is followed by the mixture, seem to be justifiable within the limits that would be indicated by the following experimental results: vapor pressure of water in mm. mercury at 0° by static method, according to Scheel and Heuse,¹ at 25°, 23.76; at 30°, 31.83; vapor pressure by air saturation method, employing the above assumptions, at 25°, 23.7 (Lincoln and Klein²); 23.71 (Krauskopf³); 23.75 (Derby, Daniels and Gutsche⁴); at 30°, 31.80 (Perman⁵). The fact that such agreement continues good throughout a range of higher temperatures⁶ makes it unlikely that the coincidence is due to a balancing of errors. It may here be noted that no one of these workers reports the use of glass wool, asbestos or other plugs to filter their saturated air stream. The work of Galizine⁷ points to the close applicability of Dalton's law at higher temperatures and lower total pressures for water and other vapors.

Erratic Results in Measurements of Vapor-Pressure Lowering.—For purposes of molecular weight determination, W. Ostwald suggested the consideration of the weights of vapor of solvent lost by potash bulbs containing respectively (1) solution of non-volatile solute of known concentration and (2) pure solvent, when the same current of gas was passed through each in series. The development of this apparently simple method, which has not even yet been brought to a form suitable for everyday laboratory application, furnishes a most interesting history.

Walker⁸ carried out the method for the solvent water, and states explicitly that cotton-wool or asbestos plugs, introduced to catch possible suspended droplets, worked "more harm than good." Will and Bredig⁹ applied Walker's technique to alcoholic and ethereal solutions, and promised to develop the method further. That they had not done so in the interim did not deter Orndorff and Carroll¹⁰ from making the effort, some

¹ *Ann. Physik.*, 31, 731 (1910).

² *J. Phys. Chem.*, 11, 318 (1907).

³ *Ibid.*, 14, 489 (1910).

⁴ *THIS JOURNAL*, 36, 793 (1914).

⁵ *Proc. Roy. Soc.*, 72, 72 (1903).

⁶ Cf. Perman, *loc. cit.*

⁷ *Ann. Physik.*, 41, 588, 770 (1890).

⁸ *Z. phys. Chem.*, 2, 602 (1888).

⁹ *Ber.*, 22, 1084 (1889).

¹⁰ *J. Phys. Chem.*, 1, 753 (1897).

years later, to adapt the method to laboratory practice. In discussing erratic results, they sense the presence of some disturbing factor other than defective saturation of the air current, and suggest surface tension. They promise further work. Speyers,¹ who wished to determine molecular weights in water and other solvents, frankly abandoned his unsuccessful attempts to use this procedure. But the method is full of fascination, and Carveth and Fowler,² in 1904, again made the attempt to improve the technique and render the results reliable. They are surprised that this method of molecular weight determination has not found favor with organic chemists, as it involves only the most common of laboratory appliances, and they suspect that such others as attempted it with unsatisfactory results must have failed to publish. Using a series of 3 water saturator tubes of Benedict's type³ containing glass wool, and later, glass beads, they were disconcerted to find the second saturator tube gaining instead of losing weight in both instances, while the third, control tube, which should have remained constant, lost much more than the second gained. The reasons for this behavior should become clear in the light of the experimental results recorded below, and one can well agree with Carveth and Fowler that the anomaly does not necessarily arise from unequal temperature. They feared especially that saturation had not been attained by previous workers. Although they took pains to guard against this source of error, they were much dissatisfied with their results, and state that "the subject may be taken up at a later date." As in the case of the other workers, however, they do not seem to have published further results.

In regard to the completeness of saturation of an air-current of reasonable speed by water vapor under the experimental conditions that have obtained with most workers, it may be stated that the observations of Perman,⁴ Lincoln and Klein,⁴ Krauskopf⁴ and others are altogether reassuring. The difficulty has, in reality, lain, not in saturating the gas-current, but in keeping it saturated until it entered the absorption vessel.

Washburn and Heuse⁵ report the use of no glass wool or other filter between saturator and absorber. They evaporated and condensed over 10 g. of water in a 24-hour run, and obtained 0.5% concordance. As is obvious from the curves below, the transfer of such large weights of water tends to diminish greatly the error due to premature condensation. Their apparatus is somewhat elaborate.

Erratic Results in Measurements of Dissociation Pressure.—The gas current saturation method has not hitherto had a very wide applica-

¹ *J. Phys. Chem.*, 1, 766 (1897).

² *Ibid.*, 8, 313 (1904).

³ *Am. Chem. J.*, 23, 326 (1900).

⁴ *Loc. cit.*

⁵ *THIS JOURNAL*, 37, 309 (1915).

tion in this field, and it is, therefore, gratifying to observe the very recent studies made by Baxter and Lansing¹ of the use of this method. The writer also hopes to report his own procedure in the near future. Surface condensation of vapor is less to be feared when the vapor is not saturated, and reference will, therefore, be made only to the work of Partington² and Tammann.³ Each of these workers passed the same gas current through (1) powdered salt hydrate, (2) absorption tubes, (3) pure water, and (4) again absorption tubes, and, from the relative weights of vapor absorbed, obtained the relation between the dissociation pressure of the salt hydrate and the vapor pressure of water at the same temperature. The surface absorption error is here likely to be incident to the gain in weight of (4).

In 2 series of experiments on the same salt hydrate, barium chloride dihydrate, Partington obtained average results differing by 4.6%. Partington appreciates the discrepancy, but offers no explanation of it other than a mention of "irregularities." Scrutiny of Partington's description and diagram of his apparatus reveals the utilization of a plug of glass wool between the water saturator and the water absorber, which was not weighed with the latter. As the 2 series of experiments were apparently separated by a considerable interval of time, the simple explanation, in the light of the data given below, is that the content of water on the surface of the glass wool had changed in the meantime. This explanation is the more probable by reason of the very small total weights of water that passed over the glass wool—less than 4 centigrams for the sum of the earlier series of 7 experiments—in marked contrast to the use of over 10 g. per experiment, with no glass wool, in the work of Washburn and Heuse.

The lack of uniformity in Tammann's results may have other causes,⁴ but he employed an asbestos filter for his air-current of 100% humidity. Asbestos is a very much less uniform material than even glass wool, so that it is hard to establish a normal behavior for it that would apply to past performances of other samples. It is hoped, however, that the simple findings reported below may serve to remind other workers to be on their guard in using it in similar cases.

Condensation of Water Vapor on Glass Surfaces.—References to the literature of this subject may be found in the writings of Freundlich,⁵ Pettijohn⁶ and others. The investigators there referred to, however, were especially careful to clean their experimental glass surfaces, whereas those workers who have used glass wool plugs incidentally to gas current

¹ THIS JOURNAL, 42, 419 (1920).

² J. Chem. Soc., 99, 466 (1911).

³ Ann. Physik., 33, 322 (1888).

⁴ Cf. Campbell, Trans. Faraday Soc., 10, 197 (1914).

⁵ Kapillarchemie, 177, 265 (1909).

⁶ THIS JOURNAL, 45, 477 (1919).

saturation measurements refer to its use only casually, and in no case give details as to its history, character or treatment. With a view, therefore, to explaining such anomalous results as those referred to above, it appeared to be desirable to obtain data as to the fraction of the weight of saturated water vapor passing over it that is taken up by "ordinary" glass wool, and also by asbestos, under the customary conditions of such experiments.

Experimental Procedure.—Much depends on what treatment a sample of glass wool must receive in order that it shall be considered representative. Some might reason that, for the present purpose, and in the absence of any statement by the users as to special treatment, glass wool was normal and representative of its kind simply as received from the dealers. Even Drucker and Ullman,¹ in a research on the surface effect of glass in vapor density determinations, do not mention washing or steaming their glass wool, but merely drying it. For the present work, however, what was done was to place the glass wool in a small calcium chloride tube, to treat it for 10 minutes with a rapid current of wet steam at 100°, to wash it very thoroughly with distilled water, and finally to dry it at 250° for 10 minutes in a current of air. In view of the findings of Sherwood,² it was judged unfair to dry at higher temperature. The glass wool was of recent American purchase, and of unknown history and kind. Of the two samples available, "coarse" and "fine" respectively, the coarse variety was selected.

A specimen was prepared for measurement by approved though laborious sampling methods, and the diameters of 30 fibers measured under a microscope with eyepiece micrometer whose readings were evaluated by a stage micrometer ruled directly on glass. Photographically reproduced stage micrometers are often several per cent. in error, and, in view of the wide variation of fiber sizes and consequent unavoidable uncertainty of average diameter, it was especially undesirable to inject any gratuitous source of error. The average diameter was 0.00308 cm., with a "standard variation" of 0.00084 cm., giving the mean error of the mean as 0.00015 cm. The diameter of the glass wool fibers used by Drucker and Ullmann³ was 0.0019 cm.; by Parks,⁴ 0.00175 cm.; and by Leech and the writer in 1912, 0.0032 cm.

Assuming that all the surface of the glass wool is cylindrical and that the density of the glass is 2.60, one may compute that the surface of the glass wool used was about 650 sq. cm per gram. The weight of glass wool used was 1.837 g., and the total glass surface within the calcium chloride tube was thus about 1230 sq. cm.

¹ *Z. phys. Chem.*, 74, 567 (1910)

² *THIS JOURNAL*, 40, 1645 (1918)

³ *Loc. cit.*

⁴ *Phil. Mag.*, [6] 5, 517 (1903).

Air saturated with water vapor at 22° was aspirated through this glass wool tube, and the issuing water vapor collected in weighed absorption tubes. In saturating the air, it was especially necessary to avoid bubbling and consequent possible air-suspended droplets. For this reason, saturators somewhat of the Kahlenberg¹ type were utilized, and the cotton wool filtered air was aspirated over the surface of distilled water that half filled 3 horizontal tubes in series, each exposing a surface about 5×25 cm., kept practically stagnant. Thence the air passed into a conical flask, containing a few mm. depth of distilled water, above which the glass wool tube was supported. All 4 vessels were completely submerged in a very well-stirred water thermostat tank. A number of runs were made, each lasting from 3 to 30 hours; and from the gains in weight of glass wool tube and absorption tubes were computed in each case (A) the percentage of the total water vapor concerned in each run that was retained by the glass wool tube, (B) the weight of water, in mg. per sq. cm. of glass surface, present at the middle of each run, and (C) the weight of water vapor in g. that had been concerned since the beginning of the first run until the middle of the run in question in building up the water found in B.

Experimental Findings. Case of Glass Wool.—The results of 8 runs are tabulated below, using the above notation:

TABLE I.
Condensation of Saturated Water Vapor on Glass Wool at 22° .

Run No	Liters per hour.	A %	B mg./cm ²	C G.
1.	3.8	13.9	0.012	0.106
2.	1.9	4.56	0.038	0.597
3.	1.0	2.71	0.056	1.29
4.	7.4	1.59	0.076	2.67
5.	11.8	0.92	0.095	4.45
6.	5.8	0.84	0.107	6.11
7.	9.7	0.79	0.118	7.77
8.	4.0	0.79	0.127	9.15

Fig. 1 shows these results graphically in 2 curves, AB and BC, in which the values of B are abscissas in both cases. As the points observed fall reasonably well on smooth curves, it is evident that the speed of the air current, within the limits tabulated, exerts little influence on the results. No comment is necessary on the magnitude of the errors to which in this case, surface condensation is thus seen to give rise, for the figures speak for themselves. The film of condensed water in Run 8 is obviously about 1.27 microns thick, and can hardly be regarded as an "adsorbed" layer in the usual sense.

An additional datum may be drawn, in confirmation, from the careful

¹ *Science*, July 21, 1905.

work of Berkeley and Hartley.¹ In their earlier measurements of the vapor pressure from water, these observers invariably found that their absorption tube gained less water vapor than was lost by the tubes supplying the vapor—by 0.37% in an experiment at 19° which they quote as typical. In their still more elaborate later work,² they sought to minimize the amount of this troublesome discrepancy, and were led to

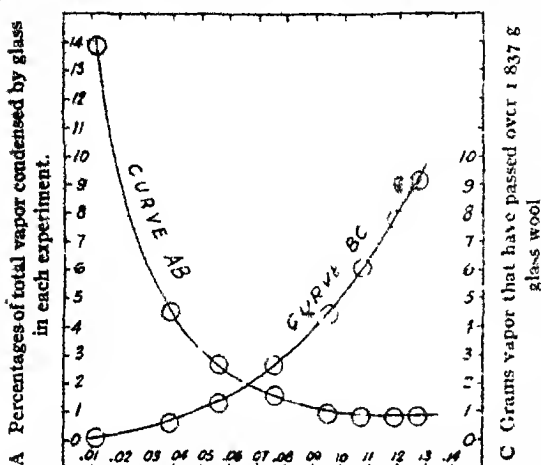


Fig. 1.—Relation of weight of water condensed on glass to (A) and (B)

area of the inner surface of the tube at 10 sq. cm, one would obtain an abscissa of 0.48 mg. for a point on curve BC with an ordinate of 350. It is well worth remarking that such skilful workers, using no glass wool and dealing with considerable weights of water vapor, are seriously but unavoidably inconvenienced by the condensation of saturated water vapor on the inner walls of a carefully cleaned short plain glass connecting tube.

Case of Asbestos.—As already indicated, it appeared hopeless to obtain what might be regarded as an average sample of asbestos on account of the enormous irregularity in several respects of various samples. A specimen of acid-washed asbestos "for Gooch crucibles" was steamed for 30 minutes, soaked in water overnight, washed with distilled water and dried in its calcium chloride tube in an air current with gentle heating. Comparing the weights of water condensed by one gram of asbestos and of glass wool on treatment at 22° with 0.63 and 2.44 g. of saturated water vapor respectively, the asbestos took up 32% and 28%, respectively, as much water as, according to curve BC, would be taken

¹ *Proc. Roy. Soc. (London)*, 77, 156 (1906).

² *Trans. Roy. Soc. (London)*, 209A, 177 (1909).

up by each gram of glass wool under like conditions. This points to a qualitative agreement in behavior of asbestos and glass wool.

Summary.

The condensation of water from its saturated vapor in air on a steamed and water-washed glass surface and on an acid-washed, steamed and water-washed asbestos surface has been investigated under the conditions that have prevailed with many users of the gas-current saturation method of vapor pressure measurement. The amount of this condensation has been found to be sufficiently great to largely account for unexplained irregularities recorded in the literature of measurements by this method.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

A SEARCH FOR AN ALKALI ELEMENT OF HIGHER ATOMIC WEIGHT THAN CESIUM.

By L. M. DENNIS AND R. W. G. WYCKOFF

Received March 22, 1920

As a result of his study of the X-ray spectra of the elements from aluminum to gold, Moseley¹ assigned atomic numbers to the elements, beginning with 13 for aluminum and closing with 79 for gold. He found known elements to correspond with all of these numbers except 3, and hence considered that there are probably 3 undiscovered elements between aluminum and gold. Siegbahn and Friman² extended the work of Moseley to the series of elements from tantalum to uranium, and found 3 unfilled places between polonium, atomic number 84, and radium, atomic number 88. The element with an atomic number of 87 would lie to the left of radium and would fall in Group 1 under cesium.

Search for this element, which may provisionally be termed eka-caesium, has already been made by Richards and Archibald,³ and by Baxter.⁴ Richards and Archibald subjected 150 g. of cesium dichloro-iodide to fractional crystallization with the object of concentrating eka-caesium, if it was present, in the fractions at one end of the series. Baxter fractionally crystallized a large amount of cesium nitrate. Neither investigation gave indication of the presence of a higher analogue of cesium.

It seemed desirable that further search for this eka-caesium be made, and that there be employed methods of fractionation involving the use of salts of cesium showing greater differences of solubility than do the

¹ *Phil. Mag.*, 27, 703 (1914).

² *Ibid.*, 32, 39 (1916).

³ *Proc. Am. Acad.*, 38, 443 (1903).

⁴ *This JOURNAL*, 37, 286 (1913).

dichloro-iodides or the nitrates. The solubilities of the nitrates of the alkalis are stated¹ to be as follows:

	Parts soluble in 100 parts water	At
KNO ₃	13 3	0°
RbNO ₃	20 1	0°
CsNO ₃	10 58	3°

If these values are correct, the nitrate of eka-caesium may be more soluble or less soluble than cesium nitrate; this uncertainty, together with the fact that the nitrates do not greatly differ in solubility, would render the search for the missing element more difficult than in the case of compounds of steadily progressing and markedly different solubility.

Experimental.

About 3500 g. of selected pollucite, containing over 30% of cesium oxide, was finely pulverized and was placed in large flasks that were fitted with reflux condensers. Conc. hydrochloric acid was added, and the contents of each flask was heated until decomposition of the mineral was complete, which required from 30 to 40 hours. The solution was diluted with water and was filtered. The filtrate was rendered slightly alkaline with ammonium hydroxide, and ammonium carbonate was added. The precipitate, which consisted chiefly of aluminum hydroxide and the carbonates of the alkaline earths, was removed by filtration, and to guard against possible loss of eka-caesium in this precipitate it was dissolved in sulfuric acid, and the alums which were thus formed were fractionated by evaporation of the solution to crystallization, discarding the mother liquor, dissolving the crystals in a small amount of hot water, cooling until crystals once more separated, and again discarding the mother liquor. This process was continued until the ammonium alum had been removed. The residual alums were later united with the alums from the sulfates, and were subjected to fractional solution, as will be described under D.

The filtrate from the precipitation of aluminum and the alkaline earths, which contained about 1250 g. of the alkalis as chlorides, was evaporated on the water bath to small bulk and the chlorides were then fractionally precipitated.

Throughout the whole investigation an arc-spectrum photograph was made of every fraction obtained by the various methods that are described below, and no material was in any case discarded until a photograph of its arc spectrum had carefully been studied.²

A. Fractional Precipitation of the Chlorides of the Alkalies.

The solubilities of the chlorides of the alkalis are stated³ to be as follows:

¹ Comey, "Dictionary of Chemical Solubilities."

² The arc spectra disclosed the presence in the mineral of an appreciable amount of vanadium.

³ Comey, *ibid.*

	Parts in 100 parts of water	At
LiCl....	63 7	0°
NaCl.....	35 7	0°
KCl.....	28 5	0°
RbCl....	76 28	1°
CsCl ...	Very deliquescent	

These data indicate that eka-caesium chloride would be more soluble in water than any other of the alkali chlorides, and that it would be concentrated in the more soluble portions if the alkali chlorides were subjected to systematic fractional precipitation. To this end, hydrogen chloride was passed into the saturated solution of the chlorides (No. 1 in the scheme shown in Fig. 1) until about 20 g. of the chlorides was precipitated. These crystals (2) were removed by filtration and were then dissolved in a little

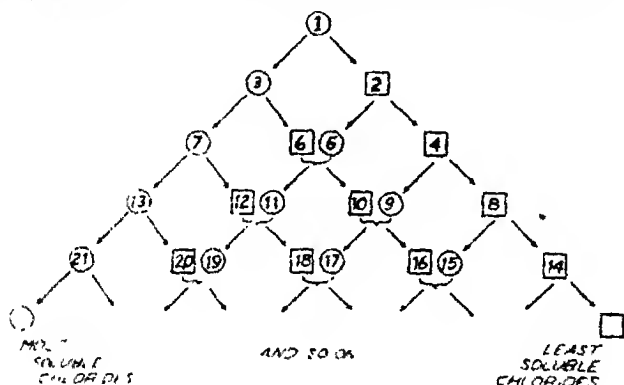


Fig. 1.

water and again precipitated by hydrogen chloride, yielding crystals (4) and mother liquor (5). The filtrate (3) from the first crop of crystals was treated with hydrogen chloride until a further precipitate (6) of about 20 g. of the chlorides resulted. Filtration yielded precipitate (6) and mother liquor (7). Precipitate (4) was dissolved in a little water and again precipitated. (5) and (6) were combined and precipitated. The fractionation was continued until 100 cc. of a saturated solution of the most soluble chlorides remained.

As the fractionation proceeded, it became necessary to concentrate the solutions. Bailey has stated¹ that when a solution of one of the alkali chlorides is boiled, a small amount of the salt passes off. The loss in the case of cesium chloride was said to be greater than with potassium chloride. Washburn and Millard, on the other hand, found that there was no loss of cesium chloride when its aqueous solution was subjected to prolonged boiling.² To avoid any possibility of the loss of eka-caesium, however,

¹ *J. Chem. Soc.*, 65, 445 (1894).

² *THIS JOURNAL*, 37, 604 (1915).

the concentration of the solutions during the fractionation was carried on under diminished pressure and the distillates were collected in flasks that contained cold water.

This fractional precipitation of the chlorides did not yield complete separation even of lithium from cesium, for the spectrum photograph of the final, most soluble portion showed that lithium was present.

Yet eka-cesium might be expected to be concentrated in this most soluble portion, and consequently this material was converted to perchlorates and was treated as described under B.

B. Fractional Solution of the Perchlorates of the Alkalies.

The saturated solution of the most soluble chlorides, mentioned in the preceding paragraph, amounted to about 100 cc. Perchloric acid was added in slight excess to $\frac{1}{2}$ this solution and the resulting precipitate of the alkali perchlorates was then subjected to fractional solution, first with portions of cold water and later with portions of hot water. About 300 cc. of water was used in each fractional treatment and the precipitate and the water was in each case thoroughly stirred by a current of air. The solution was then decanted from the precipitate and the residue was again treated with water.

This fractional solution of the perchlorates was continued until the residual, least soluble portion had been reduced to about 10 g. Arc-spectrum photographs of this residue in the red, the visible, and the ultra-violet fields showed the presence of cesium only.

C. Fractional Crystallization of the Sulfates of the Alkalies.

The solubilities of the sulfates of the alkali metals are stated¹ to be:

	Parts in 100 parts water	At
Li_2SO_4	35.34	0°
Na_2SO_4	50.2	0°; 48 parts $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 18°
K_2SO_4	21.1	15°, less at higher temp
$(\text{NH}_4)_2\text{SO}_4$	70.0	0°
Rb_2SO_4	8.5	0°
Cs_2SO_4	42.4	10°
Cs_2SO_4	158.7	-2°

These data would lead one to expect that if the sulfates were fractionally crystallized, the sulfate of eka-cesium would be concentrated in the most soluble portion.

All of the material containing the alkalies that had been extracted from the pollucite, with the exception of the small amount of alums mentioned on page 986 and the small amount of the chlorides used for the perchlorate fractionation were united. A small portion of this material containing the alkalies chiefly as chlorides was heated with conc. sulfuric

¹ Comey, *ibid.*

acid under reduced pressure in a closed apparatus, and the hydrogen chloride that was evolved was absorbed in water. This solution was examined for the presence of metallic chlorides to ascertain whether any cesium chloride (or eka-caesium chloride) passed off with the hydrogen chloride. No metallic chlorides were found in this solution and consequently all of the material was then converted to chlorides by adding conc. sulfuric acid to it and heating the solution until the hydrogen chloride was expelled. The sulfates in this resulting solution were then fractionally separated by crystallization by successive concentrations of the solution. Thallium sulfate appeared first in the least soluble fraction, together with small amounts of the sulfates of potassium, sodium, and rubidium, these being followed by large amounts of ammonium sulfate. This fractionation was continued until about 200 cc. of a saturated solution of the sulfates remained. The arc-spectrum photograph of the salt in this solution showed that only cesium was present.

D. Fractional Solution of the Alums of the Alkali Metals.

The solubilities of the aluminum alums of potassium, ammonium, rubidium and cesium are stated¹ to be as follows:

	Part in 100 parts water	At
Potassium alum.	13.5	17°
Ammonium " . . .	8.74	17.5°
Rubidium " . . .	2.27	17°
Cesium " . . .	0.619	17°

It is clear from this tabulation that the alum of eka-caesium would be less soluble than that of cesium and would probably be but very sparingly soluble in water. The solution of the last fraction of the sulfates from C was diluted and a saturated solution of aluminum sulfate was added in slight excess. This caused immediate precipitation of the alums in bulky form. The total weight of this precipitate was more than 1000 g. These alums were then fractionally dissolved by heating the precipitate with successive portions of water and vigorously stirring the solution and precipitate together while the liquid was cooling. This stirring was necessary to destroy the supersaturated solutions that these alums, particularly cesium alum, readily tend to form. One liter of water was used in the first extractions and as the amount of the residual alums gradually decreased the portions of water for the successive treatment were lessened until toward the end 100 cc. was used. After each fractional solution the cold mother liquor was poured off and the residual alums were treated with a new portion of water. The arc-spectrum photographs of the final residue showed only cesium to be present.

Summary.

The alkalis from 3500 g. of pollucite were subjected to fractionation:

A. By precipitation of the chlorides with hydrogen chloride.

¹ *Corney, ibid.*

NOTE.

B. By solution of the perchlorates.

C. By crystallization of the sulfates.

D. By solution of the alums.

In these several processes those fractions in which the higher analogue of cesium, eka-cesium, might be expected to be concentrated were examined by means of the arc spectra of the solid material in the red, the visible, and the ultra-violet portions of the spectrum. In no case were there indications of the existence of eka-cesium.

ITHACA N Y

NOTE.

Correction.—Dr. F. H. MacDougall has kindly called my attention to the fact that several errors occur in the article entitled *The Form of the Conductance Function in Dilute Solutions*, which appeared in the January, 1920, number of *THIS JOURNAL*.

Equation VII should have been written in the general form

$$\frac{d\Delta}{d(C\Delta)} = \frac{C\Delta}{K'^2} \frac{dK'}{d(C\Delta)} - \frac{1}{K'}.$$

Equation VII is in general a limiting form of this equation, which is approached as the concentration decreases. As long as $\frac{dK'}{d(C\Delta)}$ remains finite, it follows that the first term of the right-hand member will disappear at the concentration $C = 0$. In case, however, that $\frac{dK'}{d(C\Delta)}$ approaches infinity as the concentration approaches zero, the expression becomes indeterminate. In general, however, we may expect that this term will approach zero in the limit. If the value of $\frac{dK'}{d(C\Delta)}$ be substituted from Equation XV we obtain the expression

$$\frac{d\Delta}{d(C\Delta)} = \frac{Dm(C\Delta)^m}{K'^2\Delta_0^m} - \frac{1}{K'}$$

from which it follows that even though $\frac{dK'}{d(C\Delta)}$ becomes infinite as the concentration approaches the value zero, the term as a whole approaches the value zero and $\frac{d\Delta}{d(C\Delta)}$ approaches the value $-\frac{1}{K'}$. Equation VIII was intended to be written in the form

$$\frac{d^2\Delta}{d(C\Delta)^2} = \frac{dK'/d(C\Delta)}{K'^2}$$

but it is very doubtful whether this relation would be approximated even

at low concentrations. The general conclusions of the paper are not affected.

The most general expression for the first differential coefficient is

$$\frac{d\Lambda}{d(C\Lambda)} = \frac{\Lambda^2}{\Lambda_0^2 K'} \left[\frac{C\Lambda}{K'} \frac{dK'}{d(C\Lambda)} - 1 \right].$$

At low concentrations the $\Lambda, C\Lambda$ -curve will cut the Λ -axis at an angle whose tangent is equal to $-\frac{1}{K'}$. At higher concentrations the tangent to the curve will decrease because of the increase in the value of K' , as well as the increase in the value of the term involving $\frac{dK'}{d(C\Lambda)}$. The curve will, therefore, be convex toward the C -axis in dilute solutions. It is not possible to follow up the form of this curve readily at higher concentrations without introducing the equation for the conductance function. If the function XIV is introduced, we have the equation

$$\frac{d\Lambda}{d(C\Lambda)} = \frac{\Lambda^2}{\Lambda_0^2 K'} \left[m - 1 - \frac{mK}{K'} \right].$$

So long as $m < 1$, $\frac{d\Lambda}{d(C\Lambda)}$ will always have a negative value which decreases with increasing concentration. When $m > 1$, $\frac{d\Lambda}{d(C\Lambda)}$ will pass through zero and thereafter become positive at higher concentrations, which corresponds with the form of conductance curves such as we have them in solvents of low dielectric constant.

C. A. KRAUS.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

POSITIVE HALOGEN IN ORGANIC COMPOUNDS. IODINE IN DI-iodoacetylene AND CHLORO-iodo-ethylene.¹

By LLOYD B. HOWELL, with WILLIAM A. NOYES

Received February 3, 1920

For a number of years chemists have recognized the fact that certain organic halogen compounds, *e. g.*, those in which a halogen has replaced a hydrogen atom of any of the groups $-\text{NH}_2$, $>\text{NH}$, or $-\text{OH}$, exhibit extraordinary activity. Unlike the halogen of the ordinary types of alkyl and acyl halide linkage, which are reduced with more or less difficulty, the halogen of the above-mentioned types shows actual oxidizing power in the presence of such reducing agents as aqueous solutions of ferrous

¹ An abstract of a thesis submitted by Mr. Howell in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

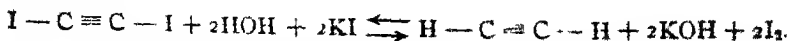
salts or metallic iodides. In addition to this exceptional property such compounds as a rule are unstable when isolated and many decompose with explosive violence. These peculiar properties have so far not been satisfactorily explained.

Inorganic halogen compounds which are similarly unstable and of oxidizing properties are the halogenated ammonias, nitrogen trichloride and nitrogen iodide. The work of Chattaway,¹ Orton, W. A. Noyes,² and others with these compounds has led to a satisfactory explanation of their behavior by the assumption that the halogen is combined as a positive atom and not negatively as in ordinary chlorides, bromides and iodides. Certainly no more reasonable explanation has so far been advanced.

It was our purpose in this investigation to determine whether or not a similar explanation might be made for the behavior of certain halogen derivatives of acetylene. In addition to the types of linkage mentioned above we have the —C—X linkage which gives relative instability to the molecule and, it will be shown, possesses oxidizing properties. Just as for many cases in the groups —NH_2 , $>\text{NH}$, and —OH the hydrogen atom may be replaced by either metals or halogen, so in acetylene or the mono-substituted acetylenes we have hydrogen replaceable by either metals or halogen. And since both the original hydrogen atom of acetylene and the metal of the acetylides or carhides are undoubtedly positive, it would seem a reasonable inference that the chlorine of chloro acetylene and dichloro-acetylene, the bromine of bromo-acetylene and dibromo acetylene, and the iodine of iodo-acetylene and di-iodo-acetylene are likewise of a positive nature.

Since it is relatively the most stable of the 6 known halogen substituted acetylenes and the easiest of preparation, di-iodo-acetylene has been investigated first for those properties which might indicate the nature of the =C-hal. linkage. Certain of the properties of this compound attributed by Nef³ to the existence of bivalent carbon in the molecule are better explained by the assumption that the iodine atoms are positive in nature and the carbon quadrivalent.

Di-iodo-acetylene when warmed with a neutral or faintly acid solution of potassium iodide or simply allowed to remain suspended in such a solution for a short time liberates free iodine and acetylene is regenerated. The rate of the reaction is very slow unless an excess of potassium iodide is present and a trace of acid added to neutralize the alkali formed in the reaction



If the iodine be taken up by titration with sodium thiosulfate it is es-

¹ *J. Chem. Soc.*, 70, 1572 (1896); *Am. Chem. J.*, 23, 363 (1900); 24, 139 (1900).

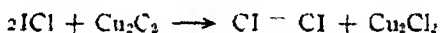
² *THIS JOURNAL*, 22, 460 (1901); 35, 767 (1913); 39, 905 (1917).

³ *Ann.*, 298, 343 (1897).

pecially noticeable that the end-point of the titration is very indistinct, more iodine being liberated almost instantly as the equilibrium is displaced. It is difficult to adopt any explanation for this reaction other than that both iodine atoms of di-iodo-acetylene are strongly electro-positive and capable of taking up 2 electrons each. That dibromo-acetylene and dichloro-acetylene recently prepared and described by Boeseken and Carriere¹ would show the same reaction even more markedly would be predicted from their relatively more unstable character. Experiments to test out these predictions are now in progress.

As a further indication of the positive character of the iodine atoms of di-iodo-acetylene, attempts have been made, first, to prepare it by means of iodine monochloride and, second, to prepare nitrogen iodide from di-iodo-acetylene by the action of ammonia. Since iodine monochloride and nitrogen iodide are both compounds containing positive iodine these reactions would furnish considerable evidence in the matter.

Iodine monochloride, however, as is well known, reacts by addition upon acetylene itself and this has been found to occur both in and out of solvents. The product always obtained is 1-chloro-2-iodo-ethylene as first shown by Plimpton.² The action of iodine monochloride upon metallo derivatives of acetylene however yields better results. Iodine monochloride with calcium carbide and with copper acetylide forms di-iodo-acetylene.



The reduction of di-iodo acetylene by ammonia has not been accomplished. The reaction has been tried out in aqueous and in ether solution and in the absence of any solvent, employing liquid ammonia itself (in which di-iodo-acetylene is readily soluble). The conditions of temperature and of pressure were likewise varied but in no case could nitrogen iodide be isolated as a product although the formation of traces of acetylene could be shown. This result might be predicted, however, since it has recently been shown by Datta and Prosad³ that nitrogen iodide is an excellent iodinating agent for acetylene and gives practically quantitative yields of tetra-iodo-ethylene. This reaction would thus seem to be only slightly reversible.

In his well-known article on "Die Chemie des Methylens," Nef⁴ has drawn the conclusion that di-iodo-acetylene and iodo-acetylene and the

¹ *Verslag. Akad. Wetenschappen, Amsterdam*, 22, 1186-88 (1914); *C. A.* 8, 3296 (1914).

² *J. Chem. Soc.*, 41, 392 (1882).

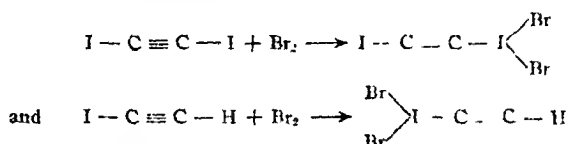
³ *THIS JOURNAL*, 39, 451 (1917).

⁴ *Loc. cit.*

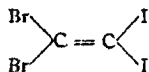
other halogen substituted acetylenes must possess the acetylidene structures:



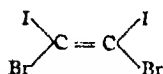
He based this conclusion in part upon the ease with which these compounds add bromine and hydrobromic acid and with which the products decompose again to give the original iodo- or di-iodo-acetylene. The possibility that these additions might be on the iodine seems not to have occurred to Professor Nef. The reactions with halogen in molecular proportions could be expressed without assuming bivalent carbon by the equations



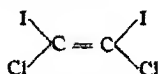
That is, the positive nature of the halogen atom as shown by its tendency to become trivalent might account for the formation of iodobromides as well as for the production of an iodochloride. In fact it is not entirely improbable that the compound $\text{C}_2\text{I}_2\text{Br}_2$, assumed by Professor Nef to be unsymmetrical,



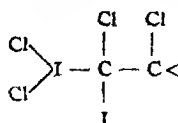
is in fact the compound,



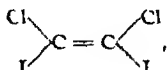
formed as a secondary or rearrangement product of the first reaction given above. The explanation for the formation of



as a secondary or rearrangement product in the chlorination of di-iodo-acetylene as given below is an analogous case. The poisonous character, disagreeable odor and irritating effects of the vapor of di-iodo-acetylene attributed by Nef to the presence of dyad carbon may possibly be due to positive or unsaturated iodine. The markedly poisonous character of the compounds nitrogen trichloride and nitrogen tri-iodide ammonia is well known. Moreover if we were to admit the compound C_2I_2 to be di-iodo-acetylidene, the structure of the iodochloride (described below) formed by the action of chlorine must be

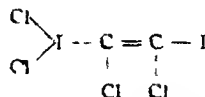


This is highly improbable since we must assume 5 halogen atoms connected to one carbon atom adjacent to a bivalent and, therefore, very reactive carbon. Moreover the decomposition of this iodochloride to give 1,2-dichloro-1,2-di-iodo-ethylene,



would be very difficult to explain.

Although it cannot yet be considered as established that the more strongly electropositive an iodine atom is, the more readily it adds chlorine to give an iodochloride, yet some evidence as to this point might be found in the fact that di-iodo-acetylene reacts with chlorine giving iodochloride-1-chloro-2,2-chloro-iodo-ethylene, Biltz¹ has reported that the product of the reaction of chlorine upon di-iodo-acetylene is hexachloro-ethane. It has been found, however, that the primary product of this reaction is the iodochloride:



This compound is formed even at ordinary temperatures in any of the solvents; ethyl chloride, ethyl bromide, chloroform or petroleum ether, and, although with much difficulty, can be isolated and analyzed. It is relatively quite unstable and decomposes in a short time with the evolution of heat. The conclusion of Biltz² that hexachloro-ethane is the product of the action of chlorine upon di-iodo-acetylene was based upon his observation of the final result of the reaction. Both iodine atoms are ultimately replaced and the bonds between the carbon atoms saturated by chlorine if the latter be allowed to react indefinitely. Hexachloro-ethane, however, is formed not by direct replacement of the iodine but by an addition to iodine first and probably the subsequent splitting out of iodine monochloride. In repeating Biltz's experiment, passing chlorine into a chloroform solution of di-iodo-acetylene (at room temperature) the iodochloride was observed to form instantly and in quantity as long, yellow needles, but in a short while these disappeared entirely and the solution became a deep brown color due to iodine monochloride. On continuing the current of chlorine deposition of crystals of iodine trichlo-

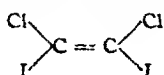
¹ Ber., 30, 1202 (1897).

² Loc. cit

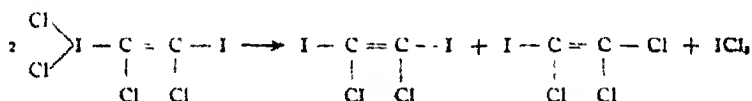
coholic potash each reacted to give di-iodo-acetylene in the case of all such compounds. Nef naturally attributed it to the comparative stability

of the group $\begin{array}{c} \text{I} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{I} \end{array}$ ^{IV} as compared with $\begin{array}{c} \text{II} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{I} \end{array}$ ^(a) _(b). It seems more reasonable to regard it as being due to the inherent positive (or basic) nature of the 2 iodine atoms. A very similar case in inorganic compounds is azoic iodide, N_2I . Abegg¹ is authority for the statement that the failure of this iodide to react with N_3Ag is the result of the positive nature of the iodine.

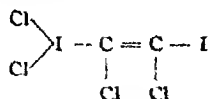
The chief product of the decomposition of iodochloride-1-chloro-2,2-chloro-iodo-ethylene is 1,2-dichloro-1,2-di-iodo-ethylene:



not previously prepared nor reported in the literature. Much iodine monochloride is liberated and traces of a second compound, an iodo-trichloro-ethylene appear to be formed. The exact nature of the decomposition is being studied further. The reaction can be shown to take place without any evolution of chlorine and indications are that its course is in part probably



1,2-dichloro-1,2-di-iodo-ethylene when treated with chlorine in ethyl chloride or petroleum ether gives also the same iodochloride,

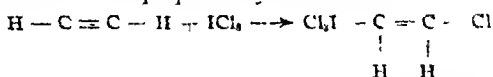


as was obtained from di-iodo-acetylene. It is always noted that decomposition of the iodochloride to give these products occurs only when the substance is either enclosed in a tube or left in a mass. Strangely enough, if some of the freshly prepared compound be spread out at once in a thin layer on a well-cooled porous plate, no darkening occurs and no liquid products form. The bright yellow color of the mass gradually fades and after about $1\frac{1}{2}$ to 2 hours a nearly white solid remains. This no longer smells of chlorine but of di-iodo-acetylene and does not liberate iodine from potassium iodide. Recrystallization and qualitative analysis show only iodine compounds present, and the m. p. is that of a mixture ($72-180^\circ$). The nature of this decomposition was not studied; it must be complex,

¹ "Handbuch der anorg. Chemie," Abt. 3, Bd. 3, S. 213.

involving that of di-iodo-acetylene into tetra-iodo-ethylene noted by V Meyer.¹

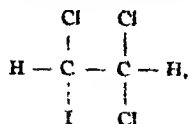
While investigating the action of iodine monochloride in hydrochloric acid as a solvent upon acetylene, occasion was had to employ crude iodine monochloride containing some iodine trichloride. This, in hydrochloric acid (1:2) solution was found to yield a small crop of fine, yellow needles of what at first seemed a stable substance. When these were removed and purification attempted they were found to decompose with the formation of liquid products deeply colored by iodine monochloride. Pure iodine trichloride was then prepared in hydrochloric acid solution and its action on acetylene tried out. The result was a very good yield of the compound, which in this case was purer and stable enough to permit its being washed, dried and analyzed. Titration by the iodometric method showed it to be an iodochloride and analysis by combustion and the method of Carius established the compound as iodochloride 2-chloro-ethylene, $\text{Cl}_2\text{I}-\text{CH}=\text{CHCl}$. As prepared by this reaction



iodochloride-chloro-ethylene is much purer and far more stable than when prepared by the method of Thiele and Haakh² from chlorine and 1-chloro-2-iodo-ethylene.

It is of theoretical interest to note here that since iodine in iodine trichloride is positive and the group $-\text{ICl}_2$ which adds to one carbon atom in acetylene is the positive group, it is very probable that the iodine atom of 1-chloro-2-iodo-ethylene is also positive. Otherwise chlorination of chloro-iodo-ethylene would, perhaps, give a different product.

It is stated by Thiele and Haakh² that this iodochloride decomposes giving chlorine and 1,2-chloro-iodo-ethylene. The observation has been made, however, that here too, as in the case of iodochloride-1-chloro-2,2-chloro-iodo-ethylene, the decomposition occurs without any increase in volume and hence with rearrangement. A number of liquid halogen compounds appear to be formed and a large amount of iodine monochloride and free iodine liberated. However, the chief product of the decomposition has been shown to be 1,2,2-trichloro-1-iodo-ethane,

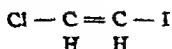


and no trace of

¹ *Ber.*, 29, 1411 (1896).

² *Ann.*, 369, 135 (1909); *Chem. Zentr.*, 1909, II, p. 2071.

³ *Ibid.*, 369, 150 (1909).



has been found. A further study of the minor decomposition products of iodochloride-2-chloro-ethylene is being made.

The addition of iodine trichloride to unsaturated hydrocarbons appears to be an excellent method for the production of aliphatic iodochlorides having chlorine on the β -carbon and its possibilities are to be investigated further.

Experimental Part.

Oxidation of Hydriodic Acid by Di-iodo-acetylene.—Di-iodo-acetylene prepared according to the method of Dehn¹ was used in all experiments. This method of preparation is to be recommended most highly over those of the older workers Berend,² Biltz³ and Nef.³ The product is practically pure and of sharp m. p. as prepared and the method is so simple and the yields so good that it leaves nothing to be desired.

In a soft, glass bomb-tube 5 millimoles (1.39 g.) of di-iodo-acetylene was covered with 10 cc. of *N* sulfuric acid (i. e., 10.0 millimoles) and 10 millimoles (1.66 g.) of *C. P.* potassium iodide, added. The pressure was reduced to 102 mm. and the bomb sealed off at the blast lamp. The tube was placed in a bomb case and immersed in a gently boiling water bath for from 8 to 10 hours. After cooling the bomb was opened by breaking the capillary within a rubber connection leading to a U-tube holding some ammoniacal cuprous chloride solution. The tube was still under reduced pressure as evidenced by bubbles of air being drawn back through the U-tube. A long glass tube reaching nearly to the liquid was introduced through a short length of rubber tubing and the connection made to the U-tube at once. On gently aspirating the gases from the bomb a fine, red precipitate of cuprous acetylide was produced in the U-tube. The test was repeated employing ammoniacal silver nitrate. The pale yellow precipitate of silver acetylide produced was partly dried and exploded in the characteristic manner on scraping with a glass rod.

The solid contents of the bomb after heating had changed over partly to a very dark brown mass of oily texture smelling strongly of unchanged di-iodo-acetylene, but consisting largely of a gray crystalline mass insoluble in water, in potassium iodide solution and in petroleum ether. This was exactly similar in all respects to the product obtained by V. Meyer and Pemsel⁴ by heating di-iodo-acetylene with water in a bomb. The liquid above the solid showed the presence of some free iodine in solution.

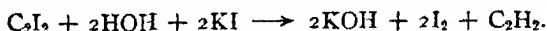
The experiment was repeated and the contents of the bomb after heating were washed out into an Erlenmeyer flask. Titration of the iodine

¹ *THIS JOURNAL*, 33, 1598 (1911).

² *Ann.*, 135, 257 (1865).

³ *Loc. cit.*

freed showed that the reaction had not proceeded far, only 1.00 cc. of 0.1 *N* sodium thiosulfate solution being taken up. The Erlenmeyer flask was connected by a stopper and glass tube to a small U-tube holding some acetone in the bend and having its outer arm closed by a Bunsen valve. The contents of the flask were now titrated for iodine at intervals for the next 11 days. Only a small fraction of a cc. of 0.1 *N* thiosulfate solution was required at any one time except in one case where the interval was 6 days, 1.51 cc being required. The end-point was followed each time in a few minutes by the color of free iodine. At the end of 11 days when the experiment was discontinued a total of 5.62 cc. of 0.1 *N* thiosulfate solution had been added. This corresponds to 0.14 millimole of di-iodo-acetylene, assuming that all of the iodine formed came from the reaction



The acetone in the bend of the tube was found to give a positive test for acetylene within 72 hours from the time the tube was connected to the flask.

Action of Iodine Monochloride upon Metallo-acetylenes. (a) *Upon Copper Acetylide*.—Pure iodine monochloride was prepared by bubbling chlorine into iodine in a side-neck test tube kept at 50–60° above a steam bath. When no further absorption occurred the tube was warmed by immersing in steam to decompose any iodine trichloride that had formed, and the product was then distilled under diminished pressure.

Copper acetylide was precipitated by treating ammoniacal cuprous chloride solution with acetylene washed by passing in the order given through (a) 1:2 nitric acid, (b) alkaline lead solution, (c) sodium hydroxide solution, (d) copper sulfate solution. The precipitate was filtered into a Gooch crucible, washed thoroughly with water and dried with alcohol and ether.

Iodine monochloride was added slowly a few drops at a time to the copper acetylide in the crucible and the mass allowed to stand a few minutes. No evidence of a violent reaction was observed. When the excess of iodine monochloride had been taken off by water and suction the odor of di-iodo-acetylene was very evident. The gray mass was now leached out thoroughly with ether, the ether extract decolorized by shaking with sodium thiosulfate solution and dried over anhydrous sodium sulfate. The ether was allowed to evaporate and a muddy white residue of characteristic odor was obtained. When taken up in alcohol (warmed to about 50–60°) and then diluted with water and cooled, very fine white needles of di-iodo-acetylene were precipitated.

(b) *Upon Calcium Carbide*.—Ordinary commercial crystalline calcium carbide was ground to a fine powder and treated with redistilled iodine monochloride a few drops at a time. The reaction was instantaneous

but not violent and much iodine was freed. Ether (or petroleum ether, b. p. 25–40°) was added and the mass thoroughly extracted. The ether extract when decolorized by sodium thiosulfate solution, washed with water and dried over anhydrous sodium sulfate, gave nearly white crystals of di-iodo-acetylene when evaporated. The characteristic odor of the product even while in solution in the ether was quite noticeable.

Action of Ammonia upon Di-iodo-acetylene. (a) *In Aqueous Solution.*—A small sample of di-iodo acetylene was introduced into a bomb tube and covered with about 2 cc. of conc. ammonium hydroxide (sp. gr. 0.90). The bomb was then sealed off, leaving a one-inch capillary. No change was apparent in the contents left at room temperature for 15 days. At the end of that time the bomb was placed in a bomb case and immersed in a steam bath for from 8 to 10 hours. As a result of this treatment the di-iodo-acetylene had disappeared and been replaced by a dark-brown mass. The liquid showed some brown color as of free iodine.

The bomb was cooled down slowly to about -10° and was opened by breaking the capillary within a rubber connection leading to a U-tube holding ammoniacal cuprous chloride solution. No test for acetylene resulted and the tube was under decidedly reduced pressure.

When the contents of the bomb were removed some of the dark solid (smelling strongly of unchanged di-iodo-acetylene) was transferred to a clay plate and dried. It was not explosive by concussion. No nitrogen iodide apparently had been formed.

(b) *In Ether Solution.*—About 0.5 g. of di-iodo-acetylene, dried over calcium chloride, was put into solution in 5 cc. of ether in a small U-tube and cooled to -8° with a freezing mixture. Dry ammonia was passed through the solution and the gas beyond allowed to bubble through a capillary U-tube containing a few drops of ammoniacal cuprous chloride solution.

In a short time an unmistakable dark-red precipitate of copper acetylide was produced in the outer tube. After a few hours of treatment with ammonia a mere trace of a brick-red solid had formed in the ether solution. When the ether had been decanted and the tube allowed to warm up the red solid decomposed rapidly but without explosion. Evaporation of the ether solution showed a brown-yellow color imparted to the large excess of di-iodo-acetylene which remained. As to the nature of the compound formed in the ether nothing can be said; acetylene was undoubtedly formed in small amounts by the reaction.

In another experiment dry ammonia was passed into a saturated solution of di-iodo-acetylene in anhydrous ether under gentle reflux. For about $\frac{1}{2}$ hour the only apparent change was the yellowing of those crystals of di-iodo-acetylene which were deposited about the inside of the delivery tube as the rapid stream of ammonia passed in. In the next few minutes

however, a very violent decomposition occurred almost explosive in nature filling the flask and connections with a dark, gray-brown deposit. This was removed and found to be largely iodine, carbon, and unchanged di-iodo-acetylene. The mass was entirely inert to concussion. The decomposition had given rise to no acetylene as shown by a U-tube holding ammoniacal cuprous chloride which had been connected to the top of the condenser.

Action of Chlorine upon Di-iodo-acetylene. Iodochloride-1,2-di-chloro-2-iodo-ethylene, $\text{Cl}_2\text{ICCl} = \text{ClCl}$.—Although other solvents such as ethyl bromide, chloroform, petroleum ether and liquid chlorine itself are found to serve, by far the best solvent in which to chlorinate di-iodo-acetylene is ethyl chloride. It is not only unacted upon by chlorine under the conditions of the experiment but its low, boiling point and the cooling effect produced by its evaporation are of much advantage.

Because of the ease with which the product decomposes it was rarely found advisable to attempt to chlorinate more than a few g. of di-iodo-acetylene at a time. In a typical preparation, where the material was *not* to be used for analysis from 3 to 8 g. of di-iodo-acetylene in from 10 to 20 cc. of ethyl chloride was employed. If the product was to be used in an analysis only a few tenths of a gram of di-iodo-acetylene in 1 to 2 cc. of solvent was used.

The solution of di-iodo-acetylene in ethyl chloride was poured into a test-tube 5×20 cm., provided with a 2-hole stopper and delivery tube (funnel-shaped end) and exit tube for the chlorine. The apparatus was cooled down to from -15° to -10° by ice and conc. hydrochloric acid and then chlorine (washed with water and conc. sulfuric acid) was passed in quite rapidly. A fleeting violet or blue coloration was at first produced, which gave way almost at once to a yellow color. In from 5 to 20 minutes bright yellow needles began to encrust the inside of the delivery tube. These increased rapidly in amount and soon formed a heavy precipitate on the sides and bottom of the tube. It was usually found best to discontinue the chlorination at the first signs of any darkening of the precipitate in the delivery tube. Otherwise both precipitate and solution rapidly turned brown indicating the replacement of iodine and the formation of iodine monochloride. In all cases where the reaction was allowed to continue to completion the crystalline precipitate slowly darkened and disappeared and was ultimately replaced by a more granular orange precipitate of iodine trichloride.

To free the crystals from any unchanged di-iodo-acetylene, iodine monochloride or hexachloro-ethane, they were washed several times by decantation with a small amount of well-cooled ethyl chloride. Material thus prepared could be kept in the dark at -15° to -10° for from 15 to 30 minutes. Exposure to light or to warmer air or reduction of the pres-

sure (lower than 50 mm.) for more than 4 or 5 minutes brought about sudden decomposition and liquefaction. The compound gives an apparent m. p. of $42-43^{\circ}$, probably rather a decomposition point, but spontaneous decomposition was found to occur, seemingly unprovoked by external conditions, at lower temperatures. The crystals were rather soluble in ether and alcohol (with some decomposition) but relatively insoluble in the solvents: chloroform, carbon tetrachloride, petroleum ether (b. p. $25-40^{\circ}$, also of b. p. $45-65^{\circ}$), ethyl bromide and ethyl chloride.

For the titrations the material as prepared above was used. A well-cooled tared glass spatula was employed to remove a small sample in a thin layer. It was held for from 30 to 40 seconds in the air (and dark) to permit any ethyl chloride to evaporate and then the sample and spatula were immersed in a weighed Erlenmeyer flask or large test-tube containing a small amount of carbon tetrachloride under potassium iodide solution which had been cooled to 0° . The gain in weight was taken as soon as the solution was at room temperature again and the iodine freed was titrated with 0.1 *N* sodium thiosulfate. Results:

	Wt sample taken G	Cc. of 0.1 <i>N</i> $\text{Na}_2\text{S}_2\text{O}_3$ required	Calc. cc 0.1 <i>N</i> $\text{Na}_2\text{S}_2\text{O}_3$ for $\text{C}_2\text{H}_4\text{CCl}_2 = \text{CCl}_4$	% oxidizing chlorine found	Theoretical % oxidizing chlorine
I	0.5677	25.92	27.04	16.2	16.88
II.	0.2039	9.45	9.71	16.41	16.88

Unless great care was taken to have the compound mixed thoroughly with the potassium iodide and carbon tetrachloride at once the available chlorine found was always lower than the theoretical. Rearrangements as already discussed evidently occurred.

For determining the total chlorine and the iodine many analyses by the methods of Carius, of decomposition with lime, and by sodium peroxide fusion were carried out. All were found to be unsatisfactory on account of the difficulty in weighing the sample without decomposition or the failure to convert all of the iodine to iodide as already discussed in the theoretical part. In the cases where decomposition with lime was attempted the tube showed free iodine when cooled after ignition even above the fusion point of the Pyrex tubing employed ($700^{\circ}-800^{\circ}$). In instances where decomposition with sodium peroxide in a Parr sulfur bomb was resorted to, the odor of di-iodo-acetylene could be noted on opening the bomb. Mixtures of magnesium filings and magnesium oxide were tested out as decomposition agents, also sodium in absolute alcohol. Both failed to decompose all of the compound, and merely converted much of it to di-iodo-acetylene.

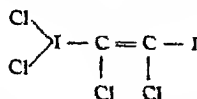
The percentage of chlorine was best determined by obtaining the ratio $\text{Cl}_2/\text{C}_2\text{I}_2$ in the case where only a small amount of the compound was prepared. The procedure was as follows:

100 mm. long with a side neck opening through the stopper was made. This together with a small funnel-end delivery tube about 80 mm. long was tared and the latter tube removed and the sample of from 0.1 to 0.3 g. of di-iodo-acetylene introduced and weighed. About one cc. of well cooled ethyl chloride was used as solvent and a slow current of chlorine was passed in (at -15° to -10° in the dark) employing the weighed delivery tube. This weight of di-iodo-acetylene treated with chlorine for from 25 to 40 minutes gave a fine light-yellow product without any darkening. At the end of this time the delivery tube was disconnected and left in the tube and the latter connected by the side neck to a filter pump so that cold (-5° to -10°) dry air could be drawn through a rather large capillary extending above the liquid to remove the ethyl chloride. In from 5 to 10 minutes the crystals could thus be freed from the solvent and excess of chlorine. Frequently sudden decomposition set in at this point, however, and ruined the experiment entirely. Where all went well the capillary was now removed and the tube closed by the glass stopper. After warming the outside by water at room temperature and opening the side neck momentarily the gain in weight was taken. This method of weighing the compound after decomposing it was, of course, based upon observations (see below) that no change of gaseous volume occurred during the transformation to the liquid.

Subs., 0.3188; 0.4719 g. iodochloride obtained Hence, 0.1531 g. of chlorine was taken up. Ratio $\frac{\text{moles of Cl}_2}{\text{moles of C}_2\text{I}_2} = \frac{2.155}{1.108}$ or 1.945.

Calc. for C_2I_2 . Cl equiv., 33.8. Found. Cl, 32.44

From the results of the titration and the per cent. of chlorine absorbed, also the fact that the compound gives di-iodo-acetylene again with alcoholic potash, we may conclude that di-iodo-acetylene under the conditions given combines with 4 atoms of chlorine, only two of which are combined to iodine and may be given up readily. This gives the structure



Spontaneous Decomposition of Iodochloride-1-chloro-2,2-chloro-iodo-ethylene. Symmetrical Chloro-iodo-ethylene.—That the spontaneous decomposition of iodochloride-1-chloro 2,2-chloro-iodo-ethylene was a rearrangement was shown by the fact that no increase or decrease of gaseous volume accompanied it. This was easily demonstrated by allowing a considerable sample of the iodochloride to decompose in a long, narrow test-tube immersed in a large graduate and closed by a one-hole stopper through which a connection was made to a small graduated (Mohr's) pipet immersed vertically beside the test-tube. The level of the water

in the latter remained practically constant as the liquefaction took place, except for a slight, temporary depression due to the sudden liberation of heat.

The first indication that decomposition had begun in a sample of iodo-chloride-1-chloro-2,2-chloro-iodo-ethylene was a slight darkening of the crystals. This was followed immediately by an appearance of sintering and the formation of crystals of iodine trichloride, then strikingly sudden liquefaction and darkening of the mass with a sharp rise in temperature.

On standing a few hours in the tube in which the change had taken place the dark brown liquid separated into 2 layers, the upper one reddish brown and transparent, and the lower one very dark violet. The upper layer was removed and found to be miscible with water and when treated with alkali gave a precipitate of iodine; sodium thiosulfate caused iodine to precipitate at first and then to dissolve in excess. These reactions indicated iodine monochloride.

It was found best not to decolorize the lower layer of the products but to subject it at once to vacuum distillation. The yield from several decompositions was combined and fractionated 3 times, once at 42-45 mm. in a 15 cc. Claisen bulb and twice at 25-26 mm. using a 5 cc. Claisen bulb. Some iodine monochloride and much free iodine came over at first and the fraction boiling at 80-90° (25 mm.) was deeply violet colored. The intermediate fractions 90-115° and 115-125° were also violet but the highest boiling and largest fraction (125-132°) distilled nearly colorless but darkened to a reddish brown color in the receiver. After a third fractionation, over 80% of the material came over at 125-132° (25-26 mm.), the bulk of it at 127.5-128.5°. Refractionation of the 3 lower fractions gave only a few drops of dark liquid, b. p. 80-84° under 32 mm. pressure.

The chief product obtained at 127.5-128.5° (25-26 mm.) was analyzed at once by the method of Carius.

Subs., 0.2381. AgCl + AgI, 0.5109, loss on heating in a stream of chlorine, 0.1241
Calc. for $C_2Cl_3I_2$: Cl, 20.34, I, 72.94. Found Cl, 19.98, I, 72.32

The compound under atmospheric pressure boils with decomposition at 243.5° (corr.) and solidifies slightly below 0°. When pure it is odorless and of pale yellow color. The halogen is precipitated with difficulty by hot alcoholic silver nitrate solution. Alcoholic potash reacts upon it to give di-iodo-acetylene.

The lower boiling liquid, of which only a small percentage was obtained, at 80-84° (32 mm.), appeared to be trichloro-iodo-ethylene. Because of the small amount and its ease of decomposition even at 26 mm. pressure, it could not be purified further. Analysis of a crude sample of 0.2176 g. gave 0.4806 g. of silver halide which in a current of chlorine lost 0.0615 g. The ratio Cl:I was thus 3.31.

Action of Chlorine upon Symmetrical Dichloro-di-iodo-ethylene.—A weighed sample of 1,2-dichloro-1,2-di-iodo-ethylene was introduced into the glass-stoppered side-neck tube used above. Employing the same method as before, the weight of chlorine taken up at -15 to -10° in ethyl chloride as a solvent was determined.

Subs., 0.1410; yellow compound, 0.1704. (Hence the ratio $\text{Cl}_2/\text{CCl}_2\text{CCl}_2 = 1.025/1.0$.)

Calc. for $\text{C}_2\text{Cl}_2\text{I}_2$: Cl taken up, 16.88. Found 17.26

That the mole of chlorine had combined to iodine to give the iodo-chloride: $\text{Cl}_2\text{I.CCl} = \text{CClI}$ and not to the carbon was shown by the reaction of the product with potassium iodide to give up one mole of chlorine again: 0.1106 g. acting on potassium iodide solution liberated iodine equivalent to 5.02 cc. of 0.1 *N* sodium thiosulfate.

Calc. for $\text{Cl}_2\text{I.CCl} = \text{CClI}$. 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$, 5.27 cc. oxidizing Cl. Found 16.1%

Calc. for iodochloride-1-chloro-2,2-chloro-iodo-ethylene 16.58%

Addition of Iodine Trichloride to Acetylene. 1-Iodochloride-2-chloro-ethylene, $\text{Cl}_2\text{ICH}:\text{CHCl}$ —From 20 to 30 cc. of a solution of iodine trichloride in conc. hydrochloric acid, prepared preferably by the method given below, was diluted with 2 volumes of ice-water. This solution was then divided among each of 3 U-tubes (Peligot type) connected in series to an acetylene generator. The tubes were immersed in water containing large pieces of ice. Acetylene (purified by washing with nitric acid (1:2), alkaline lead solution, sodium hydroxide (20%) and copper sulfate solution in the order named) was allowed to bubble through the tubes in a rapid current. After occasional shaking of the tubes the first indication of a reaction followed in from 30 to 45 minutes, fine, yellow needles of the product beginning to separate out. The current of gas was usually allowed to continue for another hour and then the product was filtered out and the filtrate returned to the tubes for the formation of a second crop of crystals. Usually the latter yield was as large as the first.

Care had to be exercised not to allow the crystals to remain in the tubes too long after forming as they were apt to become pasty or sticky and incapable of being washed. This result was evidently due to the formation of traces of chloro-iodo-ethylene by the action of some iodine monochloride present. Attempts to filter again and get out a third crop of the crystals from the filtrate always resulted in the production of chloro-iodo-ethylene instead. The latter was proven by both b. p. ($119-120^{\circ}$) and analysis. The iodochloride from the 2 crops of crystals was combined on the filter and washed quickly with ice-water 3 times and then dried by pressing well between hardened filters. If spread out at once in a thin layer it was possible to keep the product for several days, although much of it gradually disappeared and the residue became of a dirty, white color and its analysis showed a loss of chlorine. If the product was left

in a compact mass or enclosed in a tube it darkened soon and decomposed to give liquid products as discussed below. To obtain a true melting point was difficult. The temperature $61-62^{\circ}$ was the point of decomposition of the crystals when prepared from crude iodine trichloride (containing iodine monochloride) made by direct union of the elements. The same decomposition point was given for their crude product by Thiele and Haakh¹ and 75° as the true melting point for their recrystallized product. A melting point taken upon crystals freshly prepared and (recrystallized from methyl alcohol) was found to be 66° with decomposition. In other trials, however, the compound after standing for several hours showed a melting point of 80° . The compound is soluble in ether, benzene and methyl alcohol with but little decomposition for 24 hours or more but cannot be safely recrystallized from any of these except methyl alcohol.

Analyses for their product were not given by Thiele and Haakh iodo-metric titrations alone being relied upon. In the case of the present preparation it was found possible, although difficult, to analyze the crystals both by combustion and by the method of Carius. The combustion was carried out in a long 100 mm. boat and the front end of the tube was filled by a silver, spiral gauze beyond 2 boats (length 80 mm.) of molecular silver. Imperfect absorption of the halogens was otherwise found to occur. The method of Dennstedt² was tried out but was found to give incomplete absorption of the halogens even using several boats of molecular silver ahead of the sample and burning the substance very slowly. It is scarcely to be recommended for aliphatic compounds of high halogen content.

Subs. (I) 0.2260, (II) 0.1984, (III) 0.2529; H_2O (I) 0.0194, (II) 0.0147; CO_2 (I), 0.0792, (II) 0.0663; $AgI + AgCl$ (Carius) (III) 0.6409 with loss in a stream of chlorine, 0.0877.

Calc. for C_3HCl_3I : C, 9.25; H, 0.77; Cl, 41.0; I, 48.9 Found: C (I) 9.32, (II) 9.12; H (I) 0.95; (II) 0.82; Cl (III) 40.7; I, (III) 48.1.

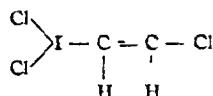
Spontaneous Decomposition of Iodochloride-2-chloro-ethylene. 1,2,2-trichloro-1-iodoethane.—In several cases when samples of iodochloride-2-chloro-ethylene were being weighed in small open weighing tubes exothermic decomposition took place and it was noted that there was no increase in the rate at which the crystals had been losing weight. For example, a sample, freshly prepared and dried as stated, was placed on the balance and weighed 0.0367 g. Gradual loss of weight occurred. After about 10 or 15 minutes sudden darkening and liquefaction took place. The same rate of decrease of weight prevailed throughout the change. After the decomposition the loss became less rapid and the total loss for the entire time was less than one mg. or 2.7%. This led to the conclusion

¹ *Loc. cit.*

² *Z. anal. Chem.*, 41, 525 (1902); *Ber.*, 41, 600 (1908).

that the change was, perhaps, a rearrangement and not a decomposition into chlorine and chloro-iodo-ethylene as reported by Thiele and Haakh. To confirm this, samples were allowed to "decompose" in a closed tube over water (method as above with iodochloride-1,2-dichloro-2-iodo-ethylene). No increase in volume accompanied the change.

A number of samples of iodochloride-2-chloro-ethylene were prepared, carefully washed and dried between hard filters and allowed to decompose in stoppered tubes immersed in water at room temperature. Within a short time after the change had occurred the liquid in each tube had separated into two layers. The upper layer proved to be iodine monochloride as shown by miscibility with water and the typical reactions with alkali and with sodium thiosulfate. The iodine monochloride represented nearly $\frac{1}{4}$ the volume of the products, approximately 12.8% of the weight of the original material or practically 1 mole of iodine monochloride to 5 moles of



taken. Boiling-point determinations made on the lower layer after its decolorization by sodium thiosulfate showed it to be a mixture. When distilled under a pressure of 23-24 mm. the boiling point rose from 40 to 120°, at which temperature decomposition occurred.

Twelve and two tenths g. of the decomposition products (lower layer) prepared as stated, was fractionated at 30-31 mm. in a long necked Claisen flask of 5 cc. capacity. Much free iodine was evolved in the first fractionation. After 3 fractionations had been made, over 42% (5.2 g.) of the products came over at 96-103° (30 mm.) and of this 2.5 to 3.0 g. boiled at 99-101.5° (30 mm.). The other fractions of consequence, 2 in number, each held approximately 15-20% of the original material but neither was large enough nor of small enough range to permit of further concentration and subsequent analysis. The low boiling material came over at 56-96° and the highest fraction at 130-145°. The latter tended to decompose to give free iodine.

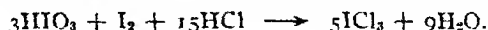
Whereas, it appeared that at least 3 compounds in addition to iodine monochloride had been formed, the chief product was that of b. p. 99-101.5° (30 mm.). It was analyzed by Carius determination and proved to be 1,2,2-trichloro-1-iodo-ethane.

Subs., 0.2405; AgI + AgCl, 0.6161; loss in a stream of chlorine, 0.0842.

Calc. for $\text{CHCl}_3\text{CHClI}$: Cl, 41.0; I, 48.9 Found. Cl, 41.2; I, 48.6.

The boiling point of pure chloro-iodo-ethylene is 27-28° under 23 mm. pressure (proven experimentally), hence it is not one of the chief products even of the decomposition of iodochloride-2-chloro-ethylene.

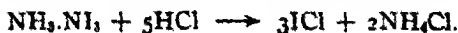
A Method of Preparation of Iodine Trichloride.—Since the usual methods for preparing iodine trichloride gave so large a proportion of iodine monochloride as to render the reagent useless in the above experiments, a new method was sought by which to prepare iodine trichloride in purer form. As it was to be used in hydrochloric acid solution a very satisfactory procedure was found to be the following, based upon the reaction



Ten and fifty-six one hundredth g. of iodic acid (3 moles) and 5.08 g. of resublimed iodine (1 mole) were ground up finely and thoroughly mixed. About twice the theoretical volume of hydrochloric acid (sp. gr. 1.19), usually 46.6 cc., was cooled down and the powdered mixture of iodine and iodic acid added in small portions with shaking. Very little chlorine was evolved and the two solids appeared to be taken up at about equal rates. All was added and dissolved giving an orange yellow solution in about 20 minutes. By employing the volume stated each cc. of the solution is theoretically equivalent to 0.5 g. of iodine trichloride. We have found that iodine trichloride in high concentrations of hydrochloric acid may be kept indefinitely at temperatures up to even 30°.

Iodine Monochloride from Nitrogen Iodide.—As being of theoretical interest iodine monochloride was prepared in hydrochloric acid solution by the reaction of conc. hydrochloric acid upon nitrogen tri-iodide. Finely powdered iodine in a Gooch crucible was digested for several minutes with ammonium hydroxide (sp. gr. 0.90). The excess of ammonium hydroxide was then drawn off and the brown mixture of iodine and nitrogen iodide washed twice with water. On adding to the mixture several cc. of conc. hydrochloric acid a sharp crackling noise gave evidence of a somewhat violent reaction. Fumes of ammonium chloride and iodine came off along with hydrochloric acid. To carry the iodine monochloride into solution excess of hydrochloric acid was now added and the clear reddish brown liquid drawn into the receiver.

This solution (a) diluted largely with water gave abrupt deepening of color as free iodine was liberated, (b) treated with sodium thiosulfate, gave a copious precipitate of iodine which redissolved in excess and (c) treated with acetylene in a U-tube gave a few globules of a heavy liquid resembling chloro-iodo-ethylene in odor and appearance (although not enough for a b. p. determination was obtained). The solution undoubtedly contained considerable iodine monochloride. The reaction was tried out merely to show that the iodine of nitrogen tri-iodide and of iodine monochloride are both of positive nature. Since hydrochloric acid is not oxidized by iodine itself the iodine monochloride must have been formed by the reaction



Summary.

1. Di-iodo-acetylene liberates iodine from aqueous solutions of iodides and acetylene is regenerated.
2. Di-iodo-acetylene reacts with ammonia giving acetylene and probably nitrogen iodide, a compound in which the iodine is positive.
3. The conduct of both iodo-acetylene and di-iodo-acetylene is best explained by the assumption that these compounds contain positive iodine, and that the structures are, respectively, $\text{H} - \text{C} \equiv \text{C} - \text{I}$ and $\text{I} - \text{C} \equiv \text{C} - \text{I}$. These structures seem at present much more probable than the acetylidene structures, $\text{IHC} = \text{C} <$ and $\text{I}_2\text{C} = \text{C} <$.
4. Biltz has reported that chlorine acts upon di-iodo-acetylene giving hexachloro-ethane. It has been shown that the primary product formed by the action of chlorine upon di-iodo-acetylene is iodochloride-1-chloro-2,2-chloro-iodo-ethylene, $\text{Cl}_2\text{I.CCl} = \text{CClI}$.
5. Iodochloride-1-chloro-2,2-chloro-iodo-ethylene decomposes very easily giving chiefly symmetrical dichloro-di-iodo-ethylene, $\text{ClCl} = \text{ClCl}$ and iodine monochloride, also probably a trichloro-iodo-ethylene.
6. The action of iodine trichloride upon acetylene gives iodochloride-2-chloro-ethylene, a compound previously prepared by Thiele and Haakh by the action of chlorine upon 1,2-chloro-iodo-ethylene. This reaction indicates that the iodine atom of chloro-iodo-ethylene is positive in nature. The addition of iodine trichloride to unsaturated linkages should be a ready method for preparing aliphatic iodochlorides having chlorine on the β -carbon.
7. The chief products formed when iodochloride-2-chloro-ethylene decomposes are iodine monochloride and 1,2,2-trichloro-1-iodo-ethane. The observation of Thiele and Haakh that 1-chloro-2-iodo-ethylene and chlorine gas result when iodochloride-2-chloro-ethylene decomposes, appears to be an error.

URBANA, ILL

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

THE MECHANISM OF THE REACTION BETWEEN KETENES
AND THE GRIGNARD REAGENT.

BY HENRY GILMAN AND L. C. HECKERT

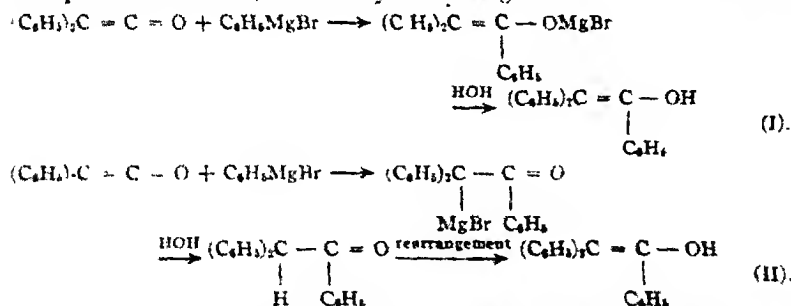
Received February 6, 1920

The characteristic grouping of the ketenes is $\overset{\textstyle |}{\text{C}} = \overset{\textstyle |}{\text{C}} = \text{O}$. Superficially they may be regarded as unsaturated ketones. However, practically all their reactions are satisfactorily explained as involving primary addition to the ethylenic linkage. A few isolated reactions have been explained by assuming addition to the carbonyl group. Staudinger and his co-workers who have given to chemistry almost all of our present

knowledge of ketenes, prefer to regard the carbonyl group in ketenes as essentially unlike the carbonyl group in aldehydes and ketones, and have explained all reactions of the ketenes on the basis of initial addition to the ethylenic linkage.

A search of the literature has disclosed the fact that there are no known cases in which the Grignard reagent combines directly with an ethylenic linkage. The work of Kohler and his co-workers,¹ Reynolds,² and Blaise and Courtot³ on the interaction of the Grignard reagent and unsaturated carbon compounds indicates an apparent addition to the ethylenic linkage. In all these cases, however, we are dealing with 1,4-addition, and the apparent 1,2-addition to the ethylenic linkage is due to the rearrangement of the enol that results when the addition product is decomposed by acids. Attempts by Blaise⁴ to bring about a reaction between the Grignard reagent and compounds having an ethylenic linkage but affording no opportunity for 1,4-addition were unsuccessful.

Apparently, then, we are concerned here with a so-called impossible reaction. On the one hand, the general reactions of ketenes demand that the Grignard reagent add to the ethylenic linkage. On the other hand, the Grignard reagent has not been known to add to an ethylenic linkage. Staudinger⁵ carried out the reaction between diphenyl ketene and phenyl magnesium bromide, and obtained triphenyl-vinyl alcohol. The formation of this compound, however, throws no light on the mechanism of the reaction. The Grignard reagent may have added either to the carbonyl group, as in the case of aldehydes and ketones, or, as Staudinger prefers to explain the reaction, to the ethylenic linkage.



Obviously the formation of triphenyl-vinyl alcohol can be explained satisfactorily by either mode of addition. It is pertinent to remark at this point, that Staudinger obtained the same product by the use of 2 or 3 molecules of phenyl magnesium bromide and the application of heat.

¹ *Am. Chem. J.*, 31, 642 (1904), etc.

* *Ibid.*, 46, 108 (1911).

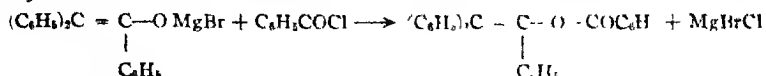
² *Compt. rend.*, 140, 370 (1905).

¹ *Ibid.*, 132, 38 (1901).

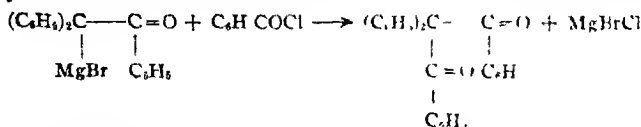
* *Ann.*, 356, 122 (1907).

The purpose of this work was to prove conclusively the mode of addition. This has been done by treating the compound resulting from the addition of diphenyl ketene and phenyl magnesium bromide with benzoyl chloride, and identifying the resulting compound.

If addition takes place as represented in (I) the magnesium addition product should give with benzoyl chloride, the benzoate of triphenylvinyl alcohol.



If addition takes place as represented in (II) the magnesium addition product should give with benzoyl chloride a 1,3 diketone, diphenyl-dibenzoyl-methane.



The product actually obtained and identified was the benzoate of triphenyl-vinyl alcohol, thereby proving that the Grignard reagent adds to the carbonyl group and not to the ethylenic linkage of ketenes. Deakin and Wilsnore¹ obtained very small amounts of acetone from the reaction between ketene and methyl magnesium iodide. Undoubtedly this reaction is to be explained by the addition of the Grignard reagent to the carbonyl group.

In view of the marked similarity in chemical behavior between ketenes and isocyanates, and because the Grignard reagent will add to a $\text{C}=\text{N}=\text{C}$ linkage, it is of interest to know the mode of addition of the Grignard reagent to isocyanates. This reaction is now being studied in this laboratory.

Experimental.

Reaction between Diphenyl Ketene and Phenyl Magnesium Bromide.

Diphenyl ketene was prepared after the method of Schroeter.³ An ethereal or petroleum ether solution of the ketene was freshly prepared for each of the several runs, the concentration being determined in the usual manner, namely, by running a measured volume of the solution into an ethereal or petroleum ether solution of aniline, and weighing the diphenyl-acetanilide formed. Because of the sparing solubility of the magnesium compounds, particularly in petroleum ether, it was found desirable to carry out the reaction in absolute ether, to use a rather dilute solution of ketene (about 0.1 *N*), and to maintain vigorous stirring throughout.

¹ *J. Chem. Soc.*, 97, 1968 (1905).

* *Ber.*, 42, 2336 (1909). See also Staudinger, *ibid.*, 44, 1619 (1911).

In a typical run the diphenyl ketene prepared in an atmosphere of carbon dioxide, was dissolved in absolute ether to make a solution of 500 cc. Using the pressure of the carbon dioxide, a measured volume of the ethereal solution was brought into immediate reaction with aniline to determine the concentration, and the remainder forced into a reaction flask. The reaction flask was a 2-liter filtering flask, immersed in a freezing mixture, and provided with a separatory funnel, mechanical stirrer, and entry tube for dry and purified hydrogen. An ethereal solution of 1.5 molecules of phenyl magnesium bromide was gradually added to the cold, vigorously stirred ethereal solution of ketene kept in a fresh atmosphere of hydrogen.

A flocculent, white precipitate soon formed and in a few runs the mixture became reddish colored. In an initial experiment the reaction mixture was directly treated with a slight excess of benzoyl chloride in absolute ether. On working up the reaction products of this run there was obtained, prior to the crystallization of the benzoate of triphenyl-vinyl alcohol, a small quantity of a sparingly soluble compound melting at 248° .¹ It was at first thought that this compound was a polymerization product of diphenyl ketene: namely, tetraphenyl-diketo-cyclobutane, a compound melting at $244-245^{\circ}$. The formation of this polymer with another was found by Staudinger to be accelerated by carbonyl containing compounds like benzoyl chloride. In consequence, the reaction mixture in subsequent runs was allowed to warm up to room temperature in the course of one hour, meanwhile being well stirred. In one of the runs, a portion of the mixture, prior to the addition of benzoyl chloride, was treated directly with dil. sulfuric acid, and triphenyl-vinyl alcohol was obtained and verified by a mixed melting-point determination.

Reaction of the Addition Compound of Diphenyl Ketene and Phenyl Magnesium Bromide with Benzoyl Chloride.—The addition compound of ketene and Grignard reagent was again cooled in a freezing mixture. To it was gradually added, with stirring, a small excess of benzoyl chloride in absolute ether. This reaction mixture, still reddish colored and containing a flocculent, white precipitate, was allowed to warm up to room temperature in the course of one hour, and then refluxed on a water-bath for 4 hours. The red color disappeared during the first half hour of heating. The ethereal mixture was cooled, treated with an excess of hydrochloric acid, and on shaking in a separatory funnel the white precipitate dissolved. The clear, slightly yellow ethereal solution was thoroughly washed, first with dil. ammonium hydroxide and then with water, dried with calcium chloride, and distilled on a water bath to drive off the ether. The resulting oil was dissolved in hot ethyl alcohol and the solution so formed allowed to cool slowly. In a few hours the solution

¹ The temperatures recorded in this paper are uncorrected.

was completely filled with white crystals melting at 143° . A single recrystallization from ethyl alcohol gave 14.7 g. of a compound melting sharply at 153° . This substance was identified as the benzoate of triphenyl-vinyl alcohol; first, by a mixed melting point determination with some of the same compound synthesized after the manner described by Biltz,¹ and second, by saponification with alcoholic potash and identification of the triphenyl-vinyl alcohol and benzoic acid so formed.

Yield of the benzoate of triphenyl-vinyl alcohol based on 10.2 g. of diphenyl ketene, 79%.

Compound Melting at 248° .—The very sparingly soluble compound formed in small quantities was crystallized from hot ethyl alcohol. It contained neither magnesium nor halogen. The compound was found to undergo no change when refluxed for 8 hours with alcoholic potash. This proved that the compound was not the supposed polymer of diphenyl ketene, tetraphenyl-diketo-cyclobutane. Staudinger and Goller² found their compound melting at $244-245^{\circ}$ to hydrolyze on even milder treatment to tetraphenyl acetone and diphenyl acetic acid.

Likewise, this proved that the compound is not diphenyl dibenzoyl methane. This compound would be expected if the Grignard reagent had added to the ethylenic linkage of the ketene. 1,3-Diketones are readily hydrolyzed under these conditions to acids and monoketones.

Summary.

The benzoate of triphenyl-vinyl alcohol was obtained when the addition compound of diphenyl ketene and phenyl magnesium bromide was treated with benzoyl chloride. This proves that the Grignard reagent adds to the carbonyl group and not to the ethylenic linkage in ketenes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE]

THE CONSTITUTION OF THE ORGANIC NITROGEN BASES OF CALIFORNIAN PETROLEUM.

BY C. F. MABERY AND L. G. WESSON

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The acid washings of crude Californian petroleum contain a mixture of organic nitrogen bases. By neutralization of the diluted acid these may be made to separate as a heavy, dark brown oil which possesses an odor closely resembling that of an empty cigar box. Californian crudes, according to Engler and Höfer,³ have the highest nitrogen content of any known petroleum, 2.39%. Japanese oil follows closely with 2.25%

¹ *Ber.*, 32, 655 (1899).

² *Ibid.*, 44, 530 (1911).

³ "Das Erdöl," I, 1913.

nitrogen, and Algerian with 2.17%, but, in general, 1.5% is the maximum found. Thus, on the basis of an average molecular weight, there may be as high as 20% of the crude oil composed of organic nitrogenous bases.¹

The problem of isolating individual bases is, however, no easy task. The mixture of compounds resembles petroleum itself in containing what are apparently whole series of related, homologous substances which can be only approximately separated by many repeated fractional distillations *in vacuo*.

In 1890 careful distillations were carried out by one of the authors on the basic constituents of a Santa Paula, California, oil.² The final main fractions, obtained by distillation under 50 to 90 mm. pressure were, according to analysis and molecular weight determinations as follows:

Fraction 130-40° as $C_{15}H_{11}N$

Fraction 197-99° as $C_{15}H_{14}N$

Fraction 209-11° as $C_{16}H_{15}N$

Fraction 215-17° as $C_{16}H_{18}N$

Fraction 223-25° as $C_{17}H_{19}N$

Fraction 270-75° as $C_{17}H_{21}N$

Chlopin concluded³ that the nitrogen bases of Galician oil consist of a "whole series of substances which have similar properties such as do homologous members of a chemical group," after the analyses of a series of fractionally precipitated double chloroplatinates of the bases.

Very briefly, the previous chemical knowledge of these basic petroleum constituents may be summarized as follows. They form illy-defined precipitates from acid solution with platinum, palladium, mercuric, cadmium, and ferric chlorides, potassium dichromate, ferro- and ferricyanides, and picric and oxalic acids. By oxidation with potassium permanganate in alkaline solution the nitrogen of the bases is evolved in part as ammonia and in part as free nitrogen. Oxidation with chromic acid forms free nitrogen and, in some cases, a small amount of acetic acid. Ethyl iodide adds to the bases if heated with them in a sealed tube. The bases are volatile with steam; they have an odor variously described as "pyridine-," "quinoline-," and "nicotine-like;" they possess rather weakly basic qualities; and, while nearly immiscible with water, they dissolve readily in alcohol, ether, benzol, carbon disulfide, etc.

The conclusion was drawn by Mabery⁴ in 1900 from as much data as was at that time obtained, that the bases of Californian petroleum consist of more or less hydrogenated quinolines, for example, tetrahydroquinoline. The experimental facts described in the following show: (1) that by the

¹ C. F. Mabery, *THIS JOURNAL*, 28, 426 (1906).

² C. F. Mabery, *J. Soc. Chem. Ind.*, 19, 505 (1900).

³ *Ber.*, 33, 2837 (1900)

⁴ *Loc. cit.*

careful oxidation with potassium permanganate of the various members of the series of fractions obtained by the vacuum distillation of the basic mixture from Californian petroleum, *pyridine pentacarboxylic acid* and *methyl pyridine tetracarboxylic acid* are obtained; (2) that no aliphatic acid is formed in an appreciable amount by this permanganate oxidation, and that the very small quantity (trace) which is actually produced has only the properties of the lowest aliphatic acids and not those of butyric acid or higher; (3) that by chromic acid oxidation of one of the members of the series of fractions, and subsequent dry distillation of the calcium salts of the organic acids thus formed, β -methyl quinoline is produced; (4) that by reduction of various members of the series of fractions with nascent hydrogen and with hydriodic acid, hydrogen atoms are added, and that the nitrogen atom of the molecule is thereby converted from a tertiary to a secondary atom; (5) that the elementary composition of 2 more completely purified fractions corresponds to that of alkylated quinolines (or isoquinolines); and (6) that the general chemical behavior of the bases is not contrary to that which might be expected of highly alkylated quinolines (or isoquinolines).

The conclusion is then drawn that the organic bases of Californian petroleum consist mainly of an indefinite mixture of alkylated quinolines (or isoquinolines), which, as regards the nitrogen-containing ring are completely alkylated, and the alkyl side chains of which consist of small groups only.

Experimental.

The bases from Santa Paula, California oil were fractioned in 1899, at first under atmospheric pressure, then immediately, because some decomposition was evident, under partial vacuum, so that none of the 15 or so final fractions was ever distilled under atmospheric pressure. After many careful distillations at 50 to 90 mm. pressure, 2 to 4° fractions were finally collected covering a range of 130 to 283°. The best fractions were analyzed for carbon, hydrogen and nitrogen; their molecular weights and specific gravities determined; platinum double salts prepared; and various oxidation decomposition reactions attempted, the latter mainly with negative results.

In 1916-17, when the present work was carried out, these samples were brown, viscous to very viscous liquids, one or two of the highest fractions becoming amorphous, resinous solids when cooled with ice. Some of the fractions were much lighter in color and less viscous than their immediate neighbors. The odor of all was nicotine-like. They were nearly insoluble in, and much heavier than water, but readily dissolved in alcohol, ether, acetone, chloroform, carbon disulfide, etc. They were also readily soluble in dil. and conc. acid, separating again on the addition of alkali.

Various representative fractions were first submitted to regulated oxidation by neutral permanganate, with the result that pyridine penta- and methyl-pyridine tetracarboxylic acids were formed.

The permanganate oxidations and isolation of the silver salts of the organic acids thus formed were carried out in the following way:

Three g. each of representative fractions was boiled with 2% potassium permanganate solution until the liquid became decolorized. More permanganate, in concentrated solution, was then added to the liquid, the boiling continued until decolorization again took place, and so on, until the color of the solution produced by fresh portions of permanganate disappeared only very slowly indeed. From 25 to 40 g. of permanganate according to the basic fraction used, was necessary to accomplish this result in from 2 to 3 days. A 2-liter, round-bottomed flask, provided with reflux condenser, was used. A second small tube reached to the bottom of the flask, and through this a slow current of air could be drawn to agitate the heavy precipitate, and prevent extreme bumping. The manganese dioxide and a small amount of unattacked base which always remained, were filtered off and the filtrate made somewhat acid with 2 cc. of conc. nitric acid, beyond the neutral point. The acidified liquid was reduced to a small volume by distillation, the distillate serving for the detection of any volatile acids which might have been formed by the oxidation reaction, and the residue for the non-volatile ones.

We shall consider first the identification of the latter, the non-volatile organic acids. For this purpose, the concentrated liquid was transferred to an evaporating dish and evaporated to complete dryness. The residue of dry salts was pulverized and thoroughly extracted for 3 hours with boiling alcohol in a Soxhlet apparatus. Into the alcohol passed resinous colored products, some potassium nitrate, and an organic, nitrogen-containing acid which, on the addition of a silver nitrate solution, formed a voluminous, white precipitate of the difficultly soluble silver salt. This product will be mentioned later.

That portion of the dry salt residue which had not dissolved was then freed from alcohol, and taken up in 200 cc. of hot water. To this aqueous solution is now added an excess of silver nitrate solution, which forms a white, voluminous precipitate, somewhat more soluble with increasing acidity of the solution.

To effect at least a partial purification of this precipitate, it was filtered off and dissolved, insofar as possible, in boiling hot 1% nitric acid solution. The insoluble residue which always remained in varied small amounts was filtered off. Upon cooling the hot filtered solution, a precipitate reformed, but the main portion separated only after the addition of sodium acetate to reduce the acidity. The product was now filtered off, washed, and dried to constant weight at 120-5°.

This product was examined with little hope at first that it would represent an individual product of the oxidation. When prepared, however, from the basic fractions of the most varying range and with quite radical modifications in the conditions of the reaction, quite the same analytical values were obtained.

The silver salts thus obtained were nearly white, do not darken at all upon boiling the water in which they are suspended, nor easily upon exposure to the light, nor upon heating them in a dry state to a temperature as high as 130° . They do, however, decompose explosively upon ignition. A distinct odor of pyridine, along with other aromatic odors, is produced by their decomposition, and a voluminous residue of silver and carbon is left. The explosive character of these salts made necessary the admixture of fine copper oxide powder in the analyses of them for carbon and hydrogen.

"Base 176-78 $^{\circ}$," requiring for 3 g. 30 g. of KMnO_4 , gave, from its "alcohol insoluble" product, a silver salt of the following composition: C, 16.40, 16.27; H, 0.37, 0.25; N, 2.38; Ag, 60.54, 60.51.

The silver salt similarly prepared by the oxidation of 3 g. of "Base 130-32 $^{\circ}$," requiring 28 g. KMnO_4 , contained: C, 16.43, 16.30; H, 0.40, 0.10; N, 2.25, 1.90; Ag, 60.66.

That from 3 g. of "Base 200-2 $^{\circ}$," which required 40 g. KMnO_4 for complete oxidation, contained: C, 15.62, 15.41; H, 0.18, 0.27; N, 1.61, 1.55; Ag, 59.80, 59.65.

That from 3 g. of "Base 209-11 $^{\circ}$," which required 38 g. KMnO_4 , gave: C, 16.11, 15.86; H, 0.23, 0.24; N, 1.91, 1.77; Ag, 60.59, 60.37.

The values may be tabulated as follows:

	Average %	C. %	H. %	N %	Ag. %	O. %
From Base						
	130-2 $^{\circ}$	16.37	0.25	2.08	60.66	20.64
	176-8	16.34	0.31	2.38	60.53	20.44
	200-2	15.52	0.23	1.58	59.73	22.94
	209-11	15.99	0.24	1.84	60.48	21.45
Grand average,		16.06	0.26	1.97	60.35	21.37
$\text{C}_{10}\text{HNAg}_4\text{O}_{10}$ (calc.),		16.51	0.14	1.93	59.41	22.01

$\text{C}_{10}\text{HNAg}_4\text{O}_{10}$ represents the tetra-silver salt of pyridine pentacarboxylic acid. A difference of one methyl group would cause a variation of 1.3% in the carbon content, whereas the greatest variation from the mean, and also the greatest variation of the averages from the calculated value is in the case of carbon which is 0.5%.

The silver content of an acid salt might well be expected to deviate from any exact atomic proportion. Because it was of greater importance in this case to learn the composition of the acid to which the silver atoms were combined than to know which salt of that acid might be present, the percentage of silver was deducted from 100%, and the carbon, hydrogen, nitrogen, and oxygen values for the "organic residue" calculated on that basis. This has been done for the average percentages given above.

	Average % for	C.	H.	N.	O.
"Organic residue" of product.. . . .	40.50	0.64	4.97	53.99	
$C_{10}HNO_4$ calc.	40.68	0.34	4.74	54.25	
Difference.....	-0.18	+0.30	+0.20	-0.26	

Although the analytical errors have been doubled, we find a striking closeness between the 2 sets of figures. The acid which corresponds to the silver-containing compound, insofar as one may judge from the analytical figures, may well be *pyridine pentacarboxylic acid*. A confirmation of the pyridine nucleus of this acid was accomplished by the preparation of pyridine itself from the barium salt of the same acid

Identification of the Pyridine Nucleus.—For this purpose the barium salt of the acid was prepared and dry-distilled, whereupon a distillate was obtained whose chief component was pyridine.

To obtain an aqueous solution of the acids, the same procedure as before in oxidation was followed. Barium chloride solution was added to the acidified filtrate after the addition of sodium acetate. The barium salt was a pure white, voluminous precipitate, which was dried and dry-distilled. The distillate was completely soluble in water, and possessed a strong, distinct pyridine odor. The distillate was acidified with hydrochloric acid, and warmed with an excess of sodium nitrite solution to decompose all ammonium hydroxide present. The solution was now evaporated to $\frac{1}{2}$ its volume, and distilled with an excess of conc. sodium hydroxide solution. The distillate was then redistilled once. An excess of picric acid, in alcoholic solution, was added to the solution, which was heated and then cooled. The voluminous precipitate of long, slender, yellow needles which formed, was recrystallized from hot alcohol, washed, and dried. The m. p. was found to be somewhat unsharp at 158–159°.

It appears that the m. p. of pyridine picrate is only with difficulty brought up to its maximum and correct value. Recrystallization of the picrate was, therefore, not attempted, but, instead, some was mixed with an equal amount of pyridine picrate prepared from pure pyridine and picric acid, and recrystallized from alcohol. The m. p. of the pure picrate was 160–2°, that of the mixture 158–60°, and that of the unknown picrate, as just stated, was 158–9°. It is apparent that the admixture of pyridine picrate with the unknown picrate raised, if anything, the m. p. of the latter, and that the unknown picrate did not appreciably lower the m. p. of the pure pyridine picrate when intimately mixed with it. The crystals of the 2 picrates were, moreover, indistinguishable in form from one another.

The base formed by the distillation of the barium salt of the acids which correspond to the analyzed silver salts of the acids is, therefore, identified with certainty as pyridine. This fact, in conjunction with the above

analyses, demonstrates that pyridine pentacarboxylic acid is formed by the oxidation of each of 4 representative fractions of the bases.

The Silver Salt from the Alcohol-Soluble Salt Residue.—To return now to the silver salt which had been prepared from the alcohol-soluble portion of the dried, potassium-salt residue. After reprecipitation from hot water, this silver salt gave indications, by its analysis, that it was an acid salt of methyl-pyridine tetracarboxylic acid. (See Analysis No. 1 below.)

Also, what is apparently the same compound was obtained in a somewhat different manner. The salt residue was treated twice with hydrochloric acid, and the excess acid and water again expelled. The pulverized residue was now exhaustively extracted with ether. Finally, $\frac{3}{4}$ g. in all of a viscous, yellow or brown oil was obtained which would not crystallize either on long standing or after $\frac{1}{2}$ hour in a freezing mixture. A silver compound was prepared from one of its components, however, by the addition of silver nitrate to its solution. To purify the precipitate thus formed, as much of it as possible was dissolved in boiling water, the insoluble residue filtered off hot, and the salt separated by cooling the filtrate. The product was washed and dried, at first in an oven, then, as darkening was noticed, in a vacuum desiccator to constant weight.

	Average % for	C	H	N	Ag	O
No. 1. From "alcohol-soluble" .		25.7	1.8	3.8	43.0	25.7
No. 2. From "ether-extracted" ...		25.3	1.8	3.3	44.1	25.5
Grand average		25.5	1.8	3.6	43.5	25.6
$\text{CH}_3\text{C}_5\text{H}_4\text{N}(\text{COOAg})_2 (\text{COOH})_2$ (calc.)		24.8	1.0	3.0	44.7	26.5

These figures indicate, when taken in conjunction with what has preceded, that a product is extracted from the salt residue, after oxidation, by alcohol, and after further acidification by ether, which gives the disilver salt of *methyl-pyridine tetracarboxylic acid*. It is of value to note here that the amount of this product was found to be much greater in the earlier experiments in which, as it now proves, somewhat less than the maximum amount of permanganate was used, while in the later experiments, in which the oxidation was carried further, the amount of this product was so small that it was not worth working upon.

As the results obtained in the oxidation of the bases by permanganate show that the final stage is pentacarboxy pyridine, the assumption is here reasonable, on the basis of the analytical figures, that the salt which corresponds to the alcohol- and ether-soluble portion is one of methyl-pyridine tetracarboxylic acid.

It may be mentioned here that the total weight of the *purified* silver salts obtained was about $\frac{1}{2}$ of the theoretical amount from 3 g. of the basic fractions.

The organic acids themselves, which correspond to these silver and bar-

ium salts, were obtained in the following manner: One g. of a basic fraction was oxidized by hot, dilute potassium permanganate solution as before, and the filtrate from the manganese dioxide evaporated to dryness. An excess of hydrochloric acid was now added to the residue, and it was again carried to complete dryness. The residue was now extracted a number of times with ether, and from the ether there was obtained, by evaporation, a few mg. of white, fern-like crystals. The amount could not be increased beyond this point as further ether extraction took out more and more of a brown impurity from which the crystals separated with greater and greater difficulty.

The crystals were those of an organic acid, very easily soluble in water and alcohol, but dissolving only with much difficulty in ether. The aqueous solution gave with ferrous sulfate a deep wine-red coloration which faded to yellow on the addition of ferric chloride. (All known pyridine acids possessing at least one carboxyl group in the α -position give a red color with ferrous sulfate solution.) Its hydrochloric acid solution did not precipitate platinic chloride, either with or without the simultaneous addition of alcohol. Its aqueous solution evolved carbon dioxide rapidly from silver, calcium, barium, etc., carbonates, and when filtered hot from the excess of metal carbonate, gave a precipitate of metal salt in each case on cooling. The silver salt formed a voluminous, white precipitate, the barium and calcium ones are rather more granular. The calcium salt was the more soluble, and on evaporation, thin, colorless plates of right angle cleavage separated at the edges of the concentrated solution.

A small amount of white, needle-shaped, acid crystals were obtained by extraction from the acid residue from the oxidation of "Base 142-6°." These were pressed out on a porous plate, moistened several times with a drop or two of water, and air-dried. A melting-point determination made upon them showed them to melt with darkening and gas evolution between 160 and 170°.

Although the melting points of the pyridine carboxy acids are not sufficiently definite and characteristic in general to lend themselves well to the purposes of identification, several careful attempts were made to prepare a pure sample of the organic acid through the barium and silver salts. The former was treated in solution with an amount of sulfuric acid exactly equivalent to its barium content; and the latter, finely ground, was suspended in boiling water while hydrogen sulfide gas was bubbled through the liquid for 5 hours. Only semi-liquid or amorphous products were obtained, however, in place of the acids.

No appreciable amount of aliphatic acid is formed by the permanganate oxidation. Other evidence afforded by permanganate oxidation of the bases was obtained by the examination of the distillates from the acidified

filtrates in each case. To each one was added a slight excess of alkali carbonate, and the solution was evaporated to dryness. The salt residue was decomposed by conc. hydrochloric or sulfuric acid in slight excess, and the acid solution extracted with ether, the ether evaporated, and the residue examined for acid.

The amount of carbonate required was, in all cases, very small, notwithstanding the fact that some mineral acid always distilled over, and the organic acid residue from the evaporated ether, consisting of an aqueous solution of the volatile acids, was never greater than a drop or two.

Several residues were tested with alcohol and conc. sulfuric acid for ester formation. The odor in each case tried was distinctly that of acetic ester, except in that of "Base 164-166°," of which the odor seemed to be richer, more like that of propionic or butyric ester. In no case, however, was a rancid-smelling, volatile acid obtained from these distillates; they had always the sharp, biting odor of conc. acetic acid.

There was always present, in greater or lesser amounts, an insoluble, steam-volatile product which contaminated the lighter acid. An attempt to prepare the pure *p*-toluide of the volatile fatty acid for its melting point identification was not successful, as the amount of acid was too small, and it was too impure. One can safely affirm, however, that from none of the fractions ranging from "Base 132-134°" to "Base 270-283°" were appreciable amounts of higher fatty acids formed. A molecular amount from an average base would be about $\frac{1}{3}$ g. from 3 g. of base.

These facts argue against the presence in the molecule of side-chains of any considerable length.

Chromic acid oxidation gave an organic acid product which, when distilled from lime, gave β -methyl quinoline. Potassium dichromate, added to a solution of one of the bases in sulfuric acid, precipitates a yellow, finely divided oil, which soon collects and clings to the side of the test tube as a brown, viscous mass. On warming the mixture, a peppery odor similar to that obtained by acid oxidation with permanganate is noticed.

Three g. of "Base 166-168°," dissolved in dil. sulfuric acid, was oxidized by 25 g. of chromic oxide, also contained in dil. sulfuric acid. The oxidizing agent was added in portions, the flask heated between additions, then cooled before the next treatment. At first, the double acid chromate separated upon each fresh addition, and only gradually disappeared on heating. After the oxidation, the sulfuric acid was partially neutralized with lime, the precipitate filtered off hot, lime then added to the filtrate in excess, the mixture evaporated to complete dryness, the mass pulverized, and the small amount of unattacked base remaining completely extracted out of the solid residue by ether.

The mass was then submitted to careful dry distillation. The distillate

consisted of an aqueous portion and oily drops. It was acidified, the oily drops dissolving, and boiled to a diminished bulk after the addition of an excess of sodium nitrite solution to destroy the ammonia which interferes with the identification of organic picrates. Now, by distillation with caustic, the other basic constituents were recovered, and were then converted into their picrates by the addition of an alcoholic picric acid solution. The first m. p. of the product was very unsharp, between 170 and 180° , but, after several recrystallizations from hot alcohol, it was raised to a sharp m. p. at 187 – 188° . This is, in all probability, the picrate of β -methyl-quinoline, m. p. 187° .

β -Methyl-quinoline may represent a β -methyl-carboxy quinoline which is known to be a resistant stage in the oxidation before the disruption of the quinoline nucleus in certain other cases.

Reduction of the bases converts the tertiary atom into a secondary one. Nascent hydrogen from sodium amalgam and alcohol, from zinc and acetic acid, and from tin and hydrochloric acid, as well as the action of hydriodic acid at 290 – 300° reduces the various basic fractions by hydrogen addition. As an example is the following:

22 g. of "Base 164–166°" was reduced by the use of mossy tin and conc. hydrochloric acid. The reduction occupied one day, and 200 cc. of the acid was used, 50 g. of tin being added in each portion at intervals. A large part of the hydrochloric acid was then evaporated off, the remainder neutralized with an excess of caustic, and steam-distilled. This last process was so slow that the separation was finally made by benzene extraction. The solvent was then evaporated, and the residue distilled *in vacuo*. The most constant fraction 208 – 210° , at 90 mm. was a light, reddish brown, rather mobile oil. When analyzed for its carbon and hydrogen content it gave

	C.	H.	N (dist.).
No. 1.....	83.30	9.51	
No. 2.....	82.58	9.66	
Average.....	82.94	9.74	7.32

This composition corresponds nearly to that of an alkylated quinoline, $C_{14}H_{17}N$, plus 3 or 4 hydrogen atoms. Thus, the calculated composition of the latter would be:

	C.	H.	N.
+ For $C_{14}H_{17}N$	82.75	10.35	6.90
For $C_{14}H_{20}N$	83.16	9.91	6.93
The product analyzes as	82.94	9.74	7.32

It is certain that in the reduction process some of the base escaped action because of the formation of an insoluble double compound of tin chloride and base hydrochloride. This separates from even the conc. acid, is soluble in benzene, and was found in the residues in the flask

from the above described distillation in the form of a dark brown, viscous oil, from which the tin is not to be precipitated by hydrogen sulfide.

That reduction has taken place upon the nitrogen ring and upon the nitrogen atom, is strongly indicated by a comparison of the actions of nitrous acid upon the basic fractions before and after treatment with nascent hydrogen. To a hydrochloric acid solution of one of the basic fractions before reduction, add a solution of sodium nitrite. An extremely small amount, if any, of an insoluble oil separates, and neutralization of the solution gives again the original base apparently unchanged by the reaction. Thus, its nitrogen atom is evidently a tertiary one.

If, however, a sodium nitrite solution be added to the solution, in acid, of one of the *reduced* bases, a reddish oil is formed in generous quantities which may be taken up in ether. The ether solution has a light color, and, on evaporation, a red liquid is left which is difficultly soluble in even conc. hydrochloric acid. Upon boiling this strongly acid solution for some minutes, and then making it alkaline, only a brownish oil, apparently the reformed base, separates.

The reddish oil which nitrous acid has formed gives, after it has been separated by the use of ether, the ether then washed thoroughly with dil. acid and evaporated off, a bright greenish blue product on treatment with phenol and sulfuric acid. (Liebermann's color reaction of nitroso amines.)

From all the evidence it seems that the nitrous acid forms a nitroso compound, a nitroso amine, of a base possessing one hydrogen atom attached to its nitrogen atom, and that reduction has taken place upon the nitrogen-containing ring and nitrogen atom of the base.

The elementary analysis of a redistilled basic fraction, and of an acid ferrocyanide gave carbon, hydrogen and nitrogen ratios of alkylated quinolines (or isoquinolines). 26 g. of a rather viscous fraction was distilled under reduced pressure. The largest fraction, which came over mainly between 188 and 195° at 14 mm. pressure, was yellowish in color with a very slight greenish fluorescence, and was somewhat viscid. Upon analysis it gave

Calc. for an alkylated quinoline containing 15 C atoms: C, 84.51; H, 8.92; N, 6.37.

Found: C, 85.25; H, 8.61; N, by diff., 6.14.

This analysis confirms the values given by the analysis of the same distillate collected under a lower pressure in the earlier work: C, 84.39; H, 8.97; N, 6.25, and the formula $C_{15}H_{11}N$ shown by its molecular weight 209, calculated 213.

It must be mentioned, however, that some of the lower boiling basic fractions undoubtedly contain too little hydrogen to correspond exactly in composition to an alkylated quinoline, while some of the higher boiling ones contain somewhat too much. Taken all in all, the conclusion to be

drawn from the elementary analysis of the basic fractions may be only that the average composition agrees as well as might be expected with the carbon-hydrogen ratio of an alkylated quinoline.

The second method which was used for determining the carbon-hydrogen ratio was by the analysis of the greenish colored acid ferrocyanide which is formed by the addition of potassium ferrocyanide solution to an acid solution of a base.

To 3.5 g. of "Base 196-198°" in dil. hydrochloric acid solution was added 8 g. of potassium ferrocyanide in aqueous solution. A yellow-green, finely crystalline precipitate, more soluble in hot water than in cold, was formed. This was filtered off, and washed, then dissolved in boiling water. Upon cooling the solution, a dark green, somewhat sticky precipitate formed. This was filtered off, and to the filtrate 5 cc. of conc. hydrochloric acid was added. This separated out a light yellow-green precipitate which was filtered off, washed, and dried. Analysis gave, as an average of two determinations

C, 65.31; H, 6.12; N, 19.11; Fe, 9.31.

The basic fraction used in the preparation of this acid ferrocyanide is, according to its carbon-nitrogen ratio, and molecular weight, a C_{13} base. The formula of an alkylated quinoline containing 13 carbon atoms is $C_{13}H_{13}N$, and its acid ferrocyanide, $(C_{13}H_{13}NH)_2H_2Fe(CN)_6$, would have the calculated composition C, 65.55%; H, 5.81%; N, 19.11%; Fe, 9.53%.

If the base be assumed to contain one more hydrogen atom than an alkylated quinoline, its acid ferrocyanide, $(C_{13}H_{14}NH)_2H_2Fe(CN)_6$, would contain C, 65.33%; H, 6.13%; N, 19.05%; and Fe, 9.49%. The composition of the base " C_{13} " lies, therefore, near that of the alkyl quinoline ratio $C_{13}H_{13}N$.

The gummy, dark green precipitate first mentioned, quite evidently impure, contained C, 70.5%; H, 8.1%; Fe, 8.7%.

Additional Reactions.

Bromine.—If liquid bromine be added to one of any of the bases, a vigorous reaction takes place; hydrogen bromide is evolved in large amounts, and a dark, resinous product is formed which can not be obtained in a crystalline condition.

On the other hand, if a solution of bromine in chloroform or carbon disulfide be added to one of the bases dissolved in the same solvent, no hydrogen bromide is given off; a dark brown oil separates, and much heat is evolved. The oil is slightly soluble in conc. hydrochloric acid, and more so when heated. It may be dissolved in hot alcohol, but on cooling the solvent, it again separates as an oil. Conc. sulfuric acid decomposes it with evolution of hydrogen bromide; heating does this as well. Fuming nitric acid has little or no apparent action even upon continued heating.

A brominated preparation was analyzed. The solvent, carbon disulfide, had been cooled during the addition of the bromine, and the solvent and excess bromine evaporated at the room temperature. The more brominated, less basic, product was separated from the less brominated by treating with conc. hydrochloric acid, washing with dil. hydrochloric acid and water, each time acting over a thin layer of the insoluble oil and manipulating it to get as thorough action as possible. The product was then dried in a vacuum desiccator over calcium chloride for 2 days, and analyzed by Carius' method for bromine.

The average bromine content found was 60.3%. $C_{14}H_{17}NBr_4$ is calculated to contain 61.6% of bromine ("C₁₄" because it was this fraction used, and "H₁₇" because the bromine content varies but little on variation of 2 or 3 hydrogen atoms, and this represents the quinoline ratio). It therefore appears that this product is mainly $C_{14}H_{17}NBr_4$.

The addition of bromine to quinoline in carbon disulfide solution also gives a tetrabromo-quinoline of unknown orientation, which is soluble in water and dil. acids, but, unlike this product, is easily soluble in alcohol, ether, and carbon disulfide.¹

The compound is slightly soluble in acidified water, as, on the addition of alkali to dil. acid which has been agitated with it, a fine emulsion appears. Silver nitrate solution forms silver bromide from a sample of the brominated product which has been thoroughly freed from uncombined bromine. With conc. sulfuric acid, or by heating, hydrogen bromide is freely evolved from the brominated base. The residue from which no more hydrogen bromide is evolved, does not give a silver bromide precipitate upon heating it with conc. nitric acid and thereupon diluting and adding silver nitrate solution.

Iodine.—Iodine in chloroform solution separates a brown, amorphous mass from the chloroform solution of any of the bases. This product can not be recrystallized from any solvent in a solid form. Apparently the same product is formed when hydriodic acid is used for the purpose of reducing the bases.

Hydriodic Acid.—One of the basic fractions was heated 3 hours at 290–300° with 52% hydriodic acid solution in a sealed tube. Only reduced base, as shown by test with nitrous acid on the acid-soluble portion of the product, and an iodine addition product were obtained.

Phthalic Anhydride.—Phthalic anhydride condenses with the basic fractions in what is evidently a phthalone formation. Alkylated quinolines possessing a methylene group in the α -position are known to be capable of condensation with phthalic anhydride; quinaldine, for example, α -methyl quinoline, forms in this manner phthalone itself or "quinoline yellow," $C_8H_7NCHCOCC_6H_4$.

¹ Claus and Isotel, *Ber.*, 15, 820 (1882).

The experiment with one of the petroleum bases was carried out as follows: 2 g. of a medium fraction was heated with one equiv. (1.5 g.) of phthalic anhydride and one g. of zinc chloride for 4 hours at 160–170° in an open flask on a sand bath. Without the zinc chloride the condensation did not occur, even with severe heating with a free flame. The product is a dark, resinous mass which may be crystallized from alcohol. The alcoholic solution colors cloth and paper a brilliant yellow which is fast to washing.

The action of fuming sulfuric acid and of bromine in chloroform solution regenerates phthalic acid from this condensation product.

Fuming Sulfuric Acid.—Experiments with several of the basic fractions showed that one of the lower fractions was capable of sulfonation without great difficulty, whereas a medium fraction was found to be extremely resistant.

"Base 134–136°" was heated overnight at 120–130° with an excess of fuming sulfuric acid. A portion of the acid solution was diluted with water, whereupon some very finely divided charred matter separated. The acid was neutralized with an excess of barium carbonate. During this part of the process the great emulsifying power of the solution was noted in the permanent froth acquired by shaking it. After the last addition, a small amount of free base was liberated. The solution was filtered while boiling hot, and the filtrate evaporated to a small bulk; a generous amount of thin, flat, transparent crystals of a barium sulfonate of the base separated.

To the remainder of the solution an excess of alkali was added, and the unsulfonated base extracted with ether. The unattacked base amounted to about $\frac{1}{4}$ of the weight of base originally taken.

A small quantity of a much higher boiling basic fraction, "Base 192–194°," was heated at 125 to 130° with an excess of fuming sulfuric acid for 14 hours. From the large amount of charred and recovered base, and the small amount of soluble barium sulfonate, it was evident that this higher basic fraction was much more resistant than the lower one to the action of fuming sulfuric acid.

Nitric Acid.—Fuming nitric acid reacts violently with the bases. Conc. nitric acid has no action in the cold, but apparently has some action on continued heating. Dil. nitric acid has no apparent action, either in the hot or cold.

Platinum Chloride.—Chloroplatinates of the bases were desired for identification and analysis. The hydrochloride of "Base 192–194°" forms a very finely granular, yellow precipitate with platinic chloride, which is soluble in hot, and difficultly soluble in cold water. Its m. p. was unsharp at 120–125°. On attempting to recrystallize this precipitate from hot water, decomposition was noted, and a brown, resinous sub-

stance separated. On account of the instability thus indicated these salts were not used.

The brominated base does not give a precipitate with platinum chloride.

Phosphorus Pentachloride and Potassium Permanganate on the Benzoylated and Acetylated Reduced Bases. Attempts to Break Open the Nitrogen Ring for Purposes of Orientation.—The use of phosphorus pentachloride in breaking open the nitrogen ring of piperidine and of tetrahydroquinoline and of similar compounds, after the stability of the nitrogen-containing ring has been first diminished by benzoylation of the base is the method of von Braun.¹ As an illustration of this method is the conversion, thereby, of benzoyl piperidine to benzoyl-chloro-*amyl*-amine, $C_6H_5CONH-(CH_2)_5Cl$, and to dichloro-pentane, $Cl(CH_2)_5Cl$

4.5 g. of "Base 164-166°" which had been reduced by nascent hydrogen, was shaken with 15 g. of benzoyl chloride in portions in the presence of an excess of 10% sodium hydroxide solution. At the end of the reaction ether was added, and the ether layer repeatedly washed with caustic solution, then twice with dil. hydrochloric acid and with water. A sticky, oily, sweetish-smelling, brown residue was left, which, in ether solution, was dried overnight with powdered calcium chloride. After filtration through a cotton plug, and evaporation of the ether in a vacuum desiccator, 3.2 g. of a reddish gum of a sweetish odor was left. It may be mentioned here that since the basic fractions themselves resist benzoylation, it is necessary to first reduce them for benzoylation.

According to the suggestion of von Braun, purification of this substance was not attempted at this stage. It was heated with phosphorus pentachloride without further treatment. This last operation, by chlorination, might be expected to break open the nitrogen-containing ring, the stability of which has been diminished, as von Braun showed in analogous cases, by the influence of the benzoyl group and quinquivalence of the nitrogen in an intermediate product.

The 3.2 g. of benzoylated product was heated with the calculated weight of phosphorus pentachloride to 120°. The reaction which took place was very vigorous, accompanied by gas evolution, and, after its intensity had diminished, the temperature was increased to 150 to 160° for $\frac{1}{2}$ hour. After cooling the flask, ice water was added in portions until all phosphorus halogen compounds had been decomposed. The remaining oil was treated with the smallest possible amount of hot, absolute alcohol, which dissolved it easily, but from which it did not crystallize of itself, nor by the aid of precipitants.

As no pure product could be crystallized out and identified, the decomposed, benzoylated, reduced base was investigated by oxidation with

¹ *Ber.*, 37, 2818 (1904).

permanganate. All of these results were negative in result, as were those of the oxidation by permanganate of some of the acetylated reduced bases.

Conclusion.

The chemical evidence as to the nature of these bases isolated from Californian petroleum supports the following views:

They consist mainly of alkylated quinolines (or isoquinolines).

Three alkyl groups are united to the α -, β - and γ -carbon atoms of the nitrogen-containing ring in all from the lowest to the highest members. Formation of pentacarboxy and methyl-tetracarboxy pyridine; the production of methyl-quinoline also agrees with this.

In the lowest fraction, $C_{12}H_{13}N$, since 3 side chains must be present, these must consist of 3 methyl groups, as the quinoline radical itself accounts for 9 out of the 12 carbon atoms.

Phthalone formation also requires a $-CH_2$ or a $-CH_2$ group in the α - or γ -position in the nitrogen-containing ring.

None of the alkyl groups represents a long side chain (more than 4 carbon atoms), even in the bases of high molecular weight, as indicated by the absence of propionic, butyric, or higher fatty acids in the oxidation products.

The behavior of the basic fractions with bromine, iodine, hydriodic acid, fuming sulfuric acid, platinic chloride, phthalic anhydride, nascent hydrogen, nitrous acid, acetylating and benzoylating agents, and mild and strong oxidizing agents is in entire conformity with these conclusions, and no fact was discovered which was antagonistic to them.

If the bases are then as simple substances as are the alkylated quinolines and isoquinolines, it may be asked why their identification could not follow from the preparation of simple salts as picrates, chloroplatinates, and double mercury compounds. It appears that this is because all of the fractions of the series of bases represent mixtures which can be fairly well separated into stages as regards molecular weights, but are difficult to separate into individual substances. The facts cited in experimental evidence for the character of the compounds represent what might be expected from a mixture of quinoline and possibly isoquinoline derivatives, a small part more, a small part less highly alkylated than the average, and containing perhaps a small percentage of hydrogenated nuclei or of pyridine derivatives.

* These admixtures would, no doubt, easily prevent the crystallization of the bases constituting the main portions, as these, under favorable circumstances, are difficultly enough solidified; and also would prevent the crystallization of products of reactions in which all of them might take part, or in which the products are, at best, difficult to crystallize.

The mixture of even 90% of an individual base with a total of 10% of isomers, homologs, and near homologs, would give a mixture which

OLIVER KAMM.

would have all of the properties found in the experimental work. Such a mixture might reasonably be expected to be formed in petroleum production.

CLEVELAND, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS
AND FROM THE ABBOTT LABORATORIES, OF CHICAGO, ILLINOIS.]

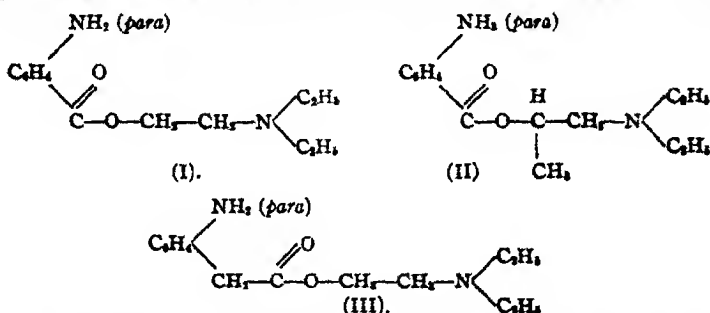
THE RELATIONSHIP BETWEEN CHEMICAL CONSTITUTION AND PHYSIOLOGICAL ACTION IN LOCAL ANESTHETICS.

I. HOMOLOGS OF PROCAINE.

BY OLIVER KAMM.

Received February 23, 1920

Several simple homologs of the well-known anesthetic, procaine (Formula I),¹ have been described in the literature. The formulas for compounds of this type which differ from the parent substance in that they possess one more carbon atom are represented structurally as follows:



Compound II is described in the German patent literature,² but the writer is not aware of published data recording the physiological action of this individual. Compound III has been synthesized more recently by Pyman³ and has been found to be inactive as an anesthetic. It is to be noted that the latter compound is an⁴ amino-alcohol ester of an aliphatic acid (*p*-aminophenyl *acetic* acid) whereas a maximum anesthetic effect appears to develop when the carbonyl group is united directly to the aromatic nucleus. Such a type of linkage is, however, not essential, provided that the carbonyl group of the ester be united to an unsaturated carbon atom,⁴ such as is illustrated by Formulas IV and V. Both of these

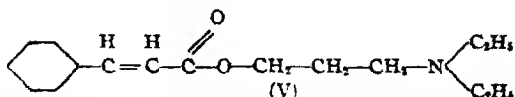
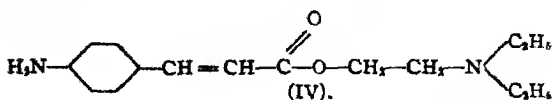
¹ This is the formula of the free base. Procaine (also called novocaine) is the monohydrochloride of this compound.

² Friedländer, 8, 995; *D. R. P.* 179,627.

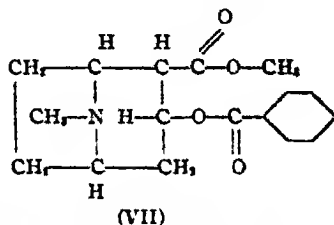
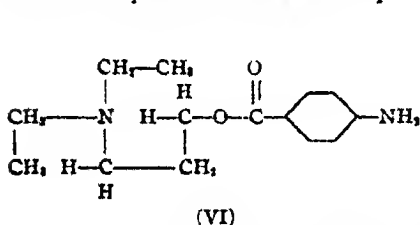
³ *J. Chem. Soc.*, 111, 167, 1119 (1917).

⁴ For exceptions see Fourneau, *J. pharm. chim.*, [7] 2, 337, 397 (1910).

compounds have been prepared¹ and found to possess anesthetic properties.



The writer has prepared a homolog of procaine possessing Structure VI. It will be noticed that this compound differs from procaine in the fact that it possesses a chain of 3 carbon atoms between the oxygen and nitrogen atoms. This variation in structure is important in the study of the relationship between chemical constitution and physiological action, because of the fact that the naturally occurring anesthetic, cocaine (VII), also possesses such a structure. The 2 formulas are here written so as to emphasize this relationship.



In physiological tests, cocaine, procaine, and the new compound (*p*-aminobenzoate of γ -diethylaminopropyl alcohol), have been tested side by side.

Aryl esters of γ -diethylaminopropyl alcohol have long been known. Thus the simplest aryl ester, the benzoyl derivative of the amino alcohol, was described by Gault² in 1908. The cinnamoyl derivative has already been referred to above (Formula V). For direct comparison with procaine it seemed advisable, however, to prepare the *p*-aminobenzoate. The method of preparation and the properties of the corresponding *m*-amino isomer are also given and a later report will deal with the study of the effects due to *ortho*-, *meta*-, and *para*-substitution.

Preparation of γ -Diethylaminopropyl Ester of *p*-Aminobenzoic Acid.

p-Nitrobenzoyl chloride (65 g.) is dissolved in 500 cc. of benzene and to this solution there is added gradually a benzene solution of 45 g. of γ -diethylaminopropyl alcohol. Reaction between the acid chloride and

¹ Friedlaender, 8, 1007; *D. R. P.* 187,593. Wildman and Thorp, U. S. pat. 1,193,649, Aug. 8, 1916.

² *Bull. soc. chim.*, [4] 3, 376, (1908).

the alcohol takes place readily with the formation of a pasty cream-colored precipitate of the hydrochloride of γ -diethylaminopropyl ester of *p*-nitrobenzoic acid. In order to insure completion of the reaction, the mixture is warmed on the water bath for about one hour, after which the precipitate is filtered off. The weight of dry product is 105 g., which corresponds closely to that theoretically possible.

The hydrochloride of γ -diethylaminopropyl ester of *p*-nitrobenzoic acid is a cream-colored solid which after one recrystallization from alcohol, melts at 189–190°. The product is dissolved in water, an excess of tin is added, and the temperature controlled at about 40° by the gradual addition of hydrochloric acid. During the first stage of the reduction an oily product separates, possibly the free nitro ester, which redissolves as the reduction proceeds. After complete reduction, the solution is diluted and the tin removed by means of hydrogen sulfide. From the clear solution the γ -diethylaminopropyl ester of *p*-aminobenzoic acid is precipitated by the addition of sodium hydroxide solution and ice. The product is a white solid which, after recrystallization from petroleum ether, melts at 69°. The yield of product corresponded to 75% of that theoretically possible. The hydrochloride of γ -diethylaminopropyl ester of *p*-aminobenzoic acid crystallizes from absolute alcohol in white needles which melt at 164°.

Preparation of γ -Diethylaminopropyl Ester of *m*-Aminobenzoic Acid.

The γ -diethyl aminopropyl ester of *m*-aminobenzoic acid may be prepared in a manner exactly analogous with that described above for the *p*-amino compound, *m*-nitrobenzoyl chloride being used in place of *p*-nitrobenzoyl chloride. The intermediate product, the γ -diethyl aminopropyl ester of *m*-nitrobenzoic acid, is obtained in the form of a hydrochloride melting at 139–140°. Upon reduction, the latter yields the γ -diethylaminopropyl ester of *m*-aminobenzoic acid, a colorless oil which solidifies only at a low temperature. Its monohydrochloride is a white solid melting at 151°, which is very soluble in water, less soluble in alcohol, and only sparingly soluble in ether.

The Relationship Between Chemical Constitution and Physiological Action in the *p*-Aminobenzoates of β -Diethylaminoethyl and γ -Diethylaminopropyl Alcohols.

The results of physiological tests that will be published in detail elsewhere¹ show that the physiological action of the *p*-aminobenzoic ester of γ -diethylaminopropyl alcohol is exactly what one might predict from its slightly closer relationship to cocaine. Procaine, Formula I, contains the structure



¹ All such references will be included in later articles in this series.

whereas, as is indicated in Formula VII, cocaine possesses a chain of 3 carbon atoms between the *N* and *O* atoms in the amino alcohol. Cocaine is considerably more toxic than procaine but for certain types of anesthesia, such as surface anesthesia, it shows stronger action than procaine because of its greater powers of penetration.

The new homologue of procaine (Formula VI) which also possesses a chain of 3 carbon atoms between the *O* and the *N* atoms of the amino-alcohol, might, therefore, be predicted to fall somewhere between procaine and cocaine in its physiological behavior, although one would expect it to be considerably more closely related to the former compound. Tests show that these predictions are entirely substantiated. The new compound is slightly more toxic than procaine; on the other hand, its effectiveness for the production of surface anesthesia is considerably greater than that possessed by its lower homolog. For certain purposes, a given result may, therefore, be obtained with a considerably smaller quantity of anesthetic, increased effectiveness more than counterbalancing the effect of slightly increased toxicity.

The writer realizes the dangers of drawing broad generalizations upon observations gathered from the testing of a small number of individual compounds, although in the present example a prediction of physiological action of a new compound predicted by analogy to structures of previously known compounds has been completely substantiated. No attempt is made, therefore, to present broader generalizations or to indulge in further speculation until a larger amount of additional experimental data is available.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF WISCONSIN AND OF VANDERBILT UNIVERSITY.]

THE PREPARATION OF *p*-PHENYLENEDIAMINE AND ANILINE FROM THEIR CORRESPONDING CHLOROBENZENES.¹

BY ARMAND J. QUICK.

Received February 23, 1920

The stability of the halogen atom attached to the benzene ring has been of considerable interest because it has prevented until recently, the direct synthesis of phenols and aromatic amino compounds from the halogen derivatives of the aromatic hydrocarbons. The early investigators² failed entirely in their efforts to replace the halogen by other groups. It was not until 1914 that Meyer and Bergius³ reported that

¹ This paper represents a part of a thesis presented by A. J. Quick to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Degree of Master of Science, June, 1919.

² *Ann.*, 104, 225 (1857); 121, 358, 362 (1862).

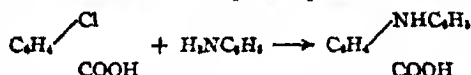
³ *Ber.*, 47, 3165 (1914).

ARMAND J. QUICK.

a dilute solution of sodium hydroxide converts chlorobenzene almost quantitatively into phenol at 300°, and that ammonia, under similar conditions, converts it partly into aniline.

It has long been known that certain negative groups, of which the nitro group is the best example, when in *ortho* or *para* position to the halogen atom have a marked labilizing effect on it. Engelhardt and Latchinow¹ as early as 1870 reported that they were able to convert *ortho* and *para* nitrochloro-benzene at least partially into their respective nitro-anilines by heating them with ammonia at 150°. In 1908 the *Aktien Gesellschaft fur Anilin Fabrikation*² took out a patent for the preparation of *p*-nitroaniline by this process. The conversion of trinitrochloro-benzene into picric acid is another illustration of the labilizing effect of the nitro group which is of commercial significance.

Ullmann³ accidentally made the discovery that metallic copper had a strong labilizing effect on nuclear halogen. While trying to condense *o*-chlorobenzoic acid with sodium phenolate in the presence of finely divided copper, Ullmann incidently used aniline as a solvent. Much to his surprise, the aniline entered into the reaction and *o*-phenyl-anthranilic acid was obtained. The reaction may be represented as follows:



This discovery opened a new field of investigation. It was soon found that *o*-chlorobenzoic acid could be condensed with phenol,⁴ thiophenol,⁵ and similar compounds under the influence of finely divided copper. Furthermore, it was found that *o*-chlorobenzoic acid could be condensed with glycine,⁶ with⁷ methylamine,⁸ and other aliphatic as well as aromatic amines and amino compounds⁷ under the influence of this catalyst.

Four years after Ullmann's discovery, a series of patents appeared which deal with the conversion of chloro-substituted benzene derivatives into aromatic amino compounds by means of ammonia in the presence of copper salts. Among these patents are listed the preparation of aniline from chlorobenzene,⁹ *p*-phenylenediamine from *p*-dichloro-benzene,⁹ and from *p*-chloro-aniline,¹⁰ *p*-phenylene-diamine-monosulfonic acid from *p*-dichloro-

¹ *Z. Chem.*, 13, [N.F VI.] 232 (1870).

² *D. R. P.* 148,749.

³ *Ber.*, 36, 2382 (1903).

⁴ *Ibid.*, 37, 853 (1904).

⁵ *Ibid.*, 37, 4526 (1904).

⁶ *Lassar-Cohn's "Arbeitsmethoden"* (4th Ed.), 601 (1907).

⁷ *D. R. P.* 145189, 146102, 146930.

⁸ *D. R. P.* 204951.

⁹ *D. R. P.* 202171.

¹⁰ *D. R. P.* 204848.

benzene-sulfonic acid,¹ and from the isomeric *p*-chloro-aniline-sulfonic acids,² and *p*-aminophenol and some of its derivatives from *p*-chlorophenol and its corresponding derivatives.³ There also appeared a patent for the preparation of diphenylamine from bromobenzene.⁴ Cuprous iodide is used in the latter patent, whereas in the other patents copper sulfate is used, the author claiming that cuprous iodide is a much more effective catalyst.

Very recently Kitamura⁵ reported that he prepared acetylaminophenol ethers by condensing acid amides with halogen substituted phenol ethers in the presence of copper as well as zinc salts.

The discovery of Ullmann has opened a wide field of investigation, but due to the fact that it had commercial possibilities, it was soon buried in patents and so found little recognition in pure synthetic organic chemistry; consequently, the information concerning the reactions already mentioned is very limited.

In this paper the action of ammonia on mono- and *p*-dichloro-benzene is studied. The objects of the work are, first, to find whether any appreciable reaction takes place; second, to study the experimental difficulties in order to ascertain whether the method is feasible for synthesis; and, third, to determine quantitatively the yields obtainable. The work was restricted to mono- and *p*-dichloro-benzene, because these were most easily prepared pure and were least liable to enter into complicated side reactions. Then, too, *p*-dichloro-benzene is a useless by-product formed in the preparation of chlorobenzene, whereas *p*-phenylenediamine, which can be obtained from it, is a valuable compound.

Experimental.

Apparatus.—The pressure bomb used for this work was made of mild steel shafting, 8.25 × 23 cm. with a boring 5 cm. in diameter and 18 cm. deep which gave it a capacity of 350 cc. and left the walls 16 mm. thick. The tube was fitted with a screw cap. Permanite, an asbestos graphite packing, was used for the gasket with very satisfactory results.

Starting Materials. *Chlorobenzene.*—This compound was prepared by the direct chlorination of benzene in the presence of anhydrous aluminum chloride which acted as a catalyzer. The compound was purified by fractional distillation and the fraction that distilled over at 131–134° was collected.

p-Dichloro-benzene was obtained from the Dow Chemical Company, Midland, Michigan. It was perfectly white and practically all distilled between 170–171° (uncorr.).

¹ D. R. P. 202564.

² D. R. P. 202563, 204972.

³ D. R. P. 203415.

⁴ D. R. P. 187870.

⁵ J. Tokyo Chem. Soc., 39, 1121–30 (1918); J. Pharm. Soc. (Japan), 1918, No. 442971.

Cuprous chloride. Merck's C. P. cuprous chloride was used.

Cuprous iodide was prepared by adding potassium iodide to a saturated copper sulfate solution, filtering off the solid cuprous iodide and finally washing it with alcohol to remove the iodine. The product was almost white.

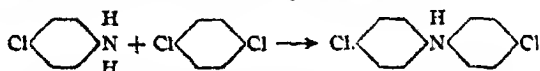
The reactions studied were primarily as represented below:



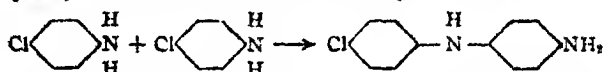
There is a possibility of other reactions taking place. Thus, the aniline formed may react with another molecule of chlorobenzene to form diphenylamine.



In the case of *p*-phenylenediamine, the possibilities are greater. One illustration will suffice. If one chlorine atom is replaced by an amino group, *p*-chloro-aniline is formed, which can react with a molecule of *p*-dichloro-benzene to form dichloro-diphenylamine.



Or it can react with a second molecule of *p*-chloro-aniline to form chlorophenyl-*p*-phenylenediamine, the reaction being as follows:



Although ammonia is used exclusively to remove the halogen, other reagents were suggested, such as sodamide, and zinc ammonium chloride. Then, too, the reaction of dilute solutions of sodium hydroxide, methyl alcoholate, and the like on chloro-substituted benzene could be studied with profit. The work is at present being continued on the mechanism of the catalysis. A number of metallic amines, especially those of bivalent cobalt, are being investigated to find whether they possess the power to activate ammonia.

Study of Catalysts.—The first problem in this work was to determine whether copper salts were the only substances that had labilizing effects on nuclear halogen. Among the other substances that were tried were salts of nickel, cobalt, and zinc. These were suggested because they form complexes with ammonia that are similar to those of copper. Then too, zinc has been reported to have catalytic properties in reactions similar to those mentioned. Since negative results were obtained in all cases, it seems that the catalytic action is not dependent on the ammonium complex. Ferrous sulfate, metallic mercury, mercuric chloride, were tried next because they possess catalytic properties in other organic reactions,

and finally sodium hydrogen sulfite was used because of its well-known power in aiding the conversion of β -naphthol into β -naphthylamine through ammonia. In all cases the results were negative.

Since copper salts showed decided catalytic properties, it seemed advisable to study the relative activities of a number of them. For this study a series of tubes, each containing a different copper salt, were run under identical conditions. Each tube contained 5 g. of *p*-dichlorobenzene, 18 cc. of conc. ammonia, and 0.5 g. of the catalyst. The set was heated at 200 to 210° for 12 hours, and after cooling the unaltered *p*-dichlorobenzene was filtered off, dried, and weighed, all other products of the reaction being soluble in water. The results were as follows:

Salt used.	Unaltered <i>p</i> -Dichloro benzene.	
	G.	%
CuI	trace
CuCl	0 15	3 0
CuCl ₂	0 70	14 0
CuSO ₄	1 15	23 0

From this it can readily be seen that the cuprous salts are more active than the cupric. Indeed there is a probability that the cupric salts only become active after reduction to the cuprous condition in the reaction mixture. This assumption seems to be borne out experimentally, for on adding potassium permanganate, which insures keeping the salt in the cupric condition, no reaction took place.

Cupric acetate and nitrate seemed to have even less catalytic power than the sulfate, although these experiments were carried out under somewhat different conditions so that exact comparisons could not be made. Metallic copper, which was prepared by reducing finely divided copper oxide with hydrogen, had no catalytic effect whatsoever.

The effect of solvents on the reaction was not studied extensively. Almost all of the reactions were carried out in aqueous solutions, although in a few cases alcohol was employed as a solvent. The alcohol was saturated with dry ammonia and the *p*-dichlorobenzene and cuprous iodide added as in the other experiments. Since not a trace of *p*-phenylenediamine was produced, it seems that catalytic effect of the copper salts is limited to aqueous solutions.

Conversion of *p*-Dichlorobenzene into *p*-Phenylenediamine.—In studying the reaction of the conversion of *p*-dichlorobenzene into *p*-phenylenediamine, the first and most important problem was the identification and quantitative determination of the latter product. Direct extraction with ether or benzene yielded some *p*-phenylenediamine, but a more satisfactory method was the dry distillation of a mixture of anhydrous sodium carbonate with the hydrochloride of the base, as recommended by Ledoux,¹ which yielded a product consisting of perfectly

¹ Ber., 7, 151 (1874).

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colorless plates having a m. p. of 138–139°, whereas the corrected m. p. is 140°. These crystals also gave the characteristic color test of *p*-phenylenediamine,¹ which is as follows: A drop of ferric chloride solution added to a dilute solution of the base or its hydrochloride will produce a deep green color which in a few seconds changes to a characteristic violet. With more concentrated solutions and boiling, a brown solution is obtained having the odor of quinone.

The yields obtained by either extraction or dry distillation were small; consequently these methods could not be employed for the quantitative estimation of the product. The most satisfactory method that was found for estimating the yields was based on the fact that *p*-phenylenediamine hydrochloride is insoluble in conc. hydrochloric acid, whereas the ammonium chloride, the copper salt, and almost all the impurities are soluble. The method of procedure in general was as follows:

The reddish blue reaction mixture, which was obtained by heating *p*-dichloro-benzene and ammonia together in the presence of a copper salt, was filtered to remove the undecomposed *p*-dichloro-benzene and other solid impurities. The mixture was then steam distilled until all the ammonia was driven off. The solution remaining in the flask was allowed to cool, then was filtered, and finally saturated with hydrogen chloride. As the solution approached saturation, crystals separated out and soon filled the container. These were filtered off, dried and weighed. As a general rule the crystals were colored reddish, and it was difficult to decolorize them. The most effective decolorizing agent found was activated charcoal, and by means of it a light gray product was obtained.

Although the product could not readily be prepared colorless, it was nevertheless fairly pure even without recrystallization as the following analysis shows:

Subs., 0.3000. AgCl, 0.4675

Calc. for $C_6H_4(NH_2)_2 \cdot 2HCl$. Cl, 39.19. Found 38.43

The sample was taken from the product obtained from Expt. 5. See Table II.

The method of analysis was as follows: The crude product was first dried in warm air, then in a desiccator over solid sodium hydroxide for 24 hours. A weighed sample of this was mixed with pure anhydrous sodium carbonate and then gently heated. After no more fumes were given off, indicating that the free base had been removed, the mass was extracted with boiling water, filtered, the filtrate acidified with nitric acid, and the silver chloride precipitated in the usual way. Besides the analysis given, others were made of the various products and the results were in almost all cases similar to the one recorded.

In the series of experiments on the preparation of *p*-phenylenediamine which will be taken up now, 3 factors were studied in particular: tem-

¹ Mulliken, "Identification of Pure Organic Compounds," 2, 112 (1916).

perature, concentration of ammonia, and the presence of mild reducing agents in conjunction with the copper salt.

TABLE I.

Expt.	Concentration of ammonia, %	Temp. °C	Undecomposed C_6H_5Cu , g	Yield of $C_6H_5(NH_2)_2$, g	$2HCl$, %
1.....	10	180-190	20	7	14
2.....	14	210	0	29	60
3.....	27	205	0	39	80

The reaction mixture in all cases consisted of 40 g of *p*-dichloro-benzene, 240 cc. of ammonium hydroxide (of the strength indicated in the table) and 5 g. of the catalyst which was cuprous iodide in No. 2 and cuprous chloride in Nos. 1 and 3. The time of heating was 18 hours.

The yields recorded are the yields obtained by saturating the solution with hydrogen chloride. It does not include the product which remained in solution, and which by experiment was found to vary from 5-8 g. in 200 cc. of solution.

Before discussing the results as set down in the table, the individual experiments will be discussed in order to bring out the details which could not be incorporated in the table.

Expt. 1 was carried out according to the procedure already given. On concentrating the solution a brick red precipitate separated which was filtered off before the solution was neutralized. This precipitate will be discussed later. The product was colored red.

Expt. 2 again yielded a little of the red precipitate, and the product was also reddish.

Expt. 3 again yielded a colored product, but no amorphous red precipitate was obtained.

Although it is difficult to draw many definite conclusions from the results given, it appears that the optimum temperature is above 200°, for below this temperature the reaction is incomplete, especially with dilute solutions of ammonia.

The yield is dependent to a certain extent on the concentration of ammonia. Thus it was found that with 5 to 6% solutions of ammonia the reaction was very incomplete even at elevated temperatures. Dilute solutions, furthermore, cause the formation of a red amorphous precipitate previously mentioned. The nature of this precipitate has not yet been intensively investigated, but from its general behavior it appears to be a condensation product. It melts with decomposition above 200°, yielding some *p*-phenylenediamine, some basic gases, and a charred mass. On exposure to air it undergoes slight oxidation and turns bluish black. It dissolves in water, producing a green solution which turns pink when acidified. It is insoluble in ether, but soluble in alcohol, and in conc. hydrochloric acid. It still contains chlorine.

It was observed that when metallic iron was added in the form of iron

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filings in conjunction with the copper salt, the solution obtained was yellow instead of red, and the product grayish white. This yellow solution when allowed to stand exposed to the air slowly turned red. Although the product was improved in appearance, the reaction was markedly retarded. With powdered aluminum the reaction was completely stopped. The results of a few typical experiments are as follows:

TABLE II.

Expt.	Reducing agent.	Conc of ammonia %.	Temp ° C.	Undecomp. $C_6H_4Cl_2$ G	Yield of $C_6H_5(NH_2)$ G	2HCl. %
1.....	Iron filings	10	220	7	32	65
2.....	Iron filings	27	190	10	13	26
3.....	Activated charcoal	27	200	0	30	61
4.....	Activated charcoal	14	200	trace	24	48
5.....	None	14	210	0	26	53

The reaction mixture consisted of 40 g. of *p*-dichloro-benzene, 240 cc of ammonium hydroxide, and 5 g. of cuprous chloride. Time 18 hrs.

Expt. 1 was run in the regular way. A reddish solution was obtained which was filtered to remove the iron and undecomposed *p*-dichloro-benzene. The latter was separated from the iron by extraction with ether. The red solution was neutralized, concentrated to 200 cc and finally saturated with hydrogen chloride. There is a possibility that the product was slightly contaminated with ammonium chloride which also crystallized out because of the high concentration of that compound due to the fact that the large excess of ammonia was not driven off but neutralized directly.

Expt. 2 yielded a yellow solution out of which a light gray product was obtained.

Expt. 3. In this experiment activated charcoal was employed. On opening the bomb, the walls were found covered with tiny leaves of metallic copper. The solution was pale yellow and gave a grayish product.

Expt. 4. This experiment was run under the same conditions as Expt. 3 except that a more dilute solution of ammonia was employed. The solution was reddish, and gave a red precipitate when it was concentrated. The product was red.

Expt. 5. This experiment was very much like Expt. 4 with the exception that no charcoal was added. The solution was red and yielded a colored product.

Again a few general conclusions can be drawn. In concentrated solutions of ammonia certain reducing agents such as iron filings and activated charcoal have a marked favorable effect on the appearance of the final product. The former, however, tends to hinder the reaction, while activated charcoal is free from this objection. These effects are not noticed in dil. ammonia solutions.

The Conversion of Chlorobenzene into Aniline.—The preparation of aniline from chlorobenzene is of greater scientific interest than it is of practical importance. Outside of the patent already mentioned in the introduction no mention of this reaction can be found in the literature.

The object of this work is to find, first, whether aniline is actually produced; second, what conditions are necessary and what yields are obtainable; and third, whether condensation such as the formation of diphenylamine takes place.

The experiments on chlorobenzene like those of dichloro-benzene, were carried out in the steel bomb at a temperature around 200°. The procedure was simple. The contents of the bomb were acidified and steam distilled, whereupon the undecomposed chlorobenzene distilled off. As soon as the distillate was clear, the distillation was stopped, and residue remaining in the flask was made alkaline with sodium hydroxide and again steam distilled. The aniline came over as a light brown oil. It was extracted with ether and dried over solid sodium hydroxide. The product was fairly pure aniline, for almost all distilled at 183°. The liquid remaining in the flask after the aniline had been steam distilled off was extracted with ether, but the extract yielded nothing, thus showing the absence of diphenylamine, for this compound is non-volatile in steam and soluble in ether. In the experiments as listed in Table III one can see that an appreciable amount of chlorobenzene is unaccounted for. Part of the loss may have been due to failure in not removing all the aniline and chlorobenzene, but other compounds may have been forming which were not isolated.

TABLE III.

50 g. of chlorobenzene was employed in every experiment.
Time of heating 18 hours.

Expt.	Ammonia used		Temp. ° C.	Undecomp C ₆ H ₅ Cl. G.	Yield of aniline		Catalyst used.
	G.	%			G.	%.	
1.....	150	25	195	9	16	39	CuSO ₄
2.....	150	27	230	0	16	39	CuCl
3.....	150	27	200	*	13	32	CuCl
4.....	150	14	200	*	14	34	CuCl
5.....	125	27	210	12	13	32	CuCl
6.....	150	27	210	40	0	0	CuI
7.....	150	14	210	30	0	0	CuI

* The chlorobenzene was not determined.

From the results as tabulated in the above table one can see that the yield is low. Expt. 1 followed the directions as given in the patent in all details except that the time of heating was 18 hours instead of 20. The patent, however, claims an 80% yield, whereas in this experiment it was found that not even half that yield was obtainable.

The concentration of ammonia between 14 and 27% seems to have no

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marked effect. The effect of temperature is greater. In order to bring about a complete decomposition of chlorobenzene a temperature higher than 200° must be employed, but even then the yield is not increased.

One striking fact brought out in Expts. 6 and 7 is that cuprous iodide does not seem to possess catalytic properties in either conc. or dil. ammonia.

As has already been mentioned, no diphenylamine could be isolated in these experiments. Since a certain patent previously discussed claims that bromobenzene and aniline react in the presence of cuprous iodide to form diphenylamine, it was considered advisable to try it out. The directions were followed exactly. A mixture of 30 parts of aniline, an excess of bromobenzene, and one part of cuprous iodide were heated for 15 hours with a reflux condenser. Little reaction took place, although the reaction mixture turned blue in color. Practically all the aniline and bromobenzene were recovered. No diphenylamine could be detected.

A similar mixture was heated under pressure in the steel bomb. Chlorobenzene, however, was used instead of bromobenzene. A temperature of 220° was maintained for 18 hours. Again no diphenylamine could be isolated.

Summary.

A number of inorganic salts, including various salts of copper have been investigated to determine their labilizing effect on the chlorine in *p*-dichlorobenzene.

p-Phenylenediamine has been prepared by the action of ammonia on *p*-dichlorobenzene in the presence of cuprous salts. The methods used for isolating the free base as well as the hydrochloride have been described.

Aniline has been obtained by the action of ammonia on chlorobenzene in the presence of a copper salt.

An attempt to condense chlorobenzene and aniline in the presence of cuprous iodide has failed.

The author takes this opportunity to express his thanks to Professors R. Fischer, L. Kahlenberg and G. L. Clark for helpful suggestions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE IDENTIFICATION OF ACIDS. V. PARA HALOGEN PHENACYL ESTERS.

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Introduction.

It has been shown by Rather and Reid² that phenacyl esters are in some cases superior to *p*-nitrobenzyl esters for the identification of acids, but in a number of cases the phenacyl esters are oils or low-melting solids. It is well known that *p*-nitro and *p*-bromophenyl hydrazones are sometimes solids when the unsubstituted hydrazones are oils. Previous work has shown that *p*-nitrobenzyl bromide is much more satisfactory than *p*-nitrobenzyl chloride on account of greater promptness and completeness of reaction with alkali salts. As *p*-nitro-acetophenone is not readily accessible, *p*-bromophenacyl bromide appeared to be the most promising reagent.

The results have confirmed this prediction. A number of *p*-bromophenacyl esters have been prepared and their properties studied. Partly for comparison, and partly to secure additional derivatives which might be of use in doubtful cases, some of the corresponding *p*-chloro- and *p*-iodophenacyl esters have also been studied.

Historical.

p-Chlorophenacyl bromide, $\text{ClC}_6\text{H}_4\text{COCH}_2\text{Br}$, or 4-chloro-1'-bromo-acetophenone was made by Collet³ by the Friedel and Craft reaction from monochlorobenzene and bromo-acetyl chloride. Later he prepared it by first making *p*-chloro-acetophenone⁴ by the Friedel and Craft reaction and then brominating the methyl group. His product melted at 96-96.5°.

p-Bromophenacyl bromide, $\text{BrC}_6\text{H}_4\text{COCH}_2\text{Br}$, or 1',4-dibromo-acetophenone, was also made by Collet by the same methods. The melting point, as observed by him, was 109-109.5°.

p-Iodophenacyl bromide, $\text{IC}_6\text{H}_4\text{COCH}_2\text{Br}$, is not described in the literature.

Of the *p*-halogenphenacyl alcohols, only the *p*-chlorophenacyl alcohol, $\text{ClC}_6\text{H}_4\text{COCH}_2\text{OH}$ (also known as *p*-chlorobenzoyl carbinol), is described in the literature. Straus⁵ first made this compound from the acetate, which is also the only *p*-halogenphenacyl ester described. Upon boiling *p*-chlorophenacyl bromide in alcoholic solution with sodium acetate and a little acetic acid, he obtained the *p*-chlorophenacyl acetate which

¹ From a dissertation by W. Lee Judefind.

² THIS JOURNAL, 41, 75 (1919).

³ *Compt. rend.*, 125, 717 (1897).

⁴ *Bull. soc. chim.*, [3] 21, 69 (1899).

⁵ *Ann.*, 303, 331 (1912).

melted at 65–66.5°. He then hydrolyzed the acetate by boiling it in water with barium carbonate. The alcohol crystallized out in needles melting at 122–3°.

Preparation of Reagents.

All 3 of the reagents were made by the second method used by Collet (*q. v.*). The materials used for their preparation were commercial products, which were redistilled until a fairly high degree of purity was obtained.

The *p*-chlorophenacyl bromide was the least difficult to prepare. It was found by experiment that for the best yield of *p*-chloro-acetophenone (of *p*-bromo- and *p*-iodo- also), the following proportions of materials are to be used: one mole of monochlorobenzene, or 112 g. (157 g. of bromobenzene, or 204 g. of iodobenzene), 85 g. of acetyl chloride (10% excess), 150 g. of anhydrous aluminum chloride (10% excess) and 250 g. of carbon disulfide as solvent. The chlorobenzene, aluminum chloride and carbon disulfide were put in a balloon flask fitted with a reflux condenser. The acetyl chloride was added through the condenser in 5 g. portions at intervals of about half an hour. In order to start the reaction it was necessary to immerse the flask in warm water for a short time, after which the reacting mixture was cooled with tap water, so that a slow evolution of hydrochloric acid occurred. If the temperature is kept low the formation of gummy products is almost entirely avoided. After the reaction was completed, *i. e.*, when the evolution of hydrochloric acid ceased, the mixture was heated on a water bath at 70–80° in order to drive off the carbon disulfide. The product was then decomposed gradually with ice water (or cracked ice). The *p* chloro-acetophenone separated as a heavy, yellow oil, which was dried and distilled under reduced pressure. The distillate was redistilled at atmospheric pressure, the portion going over between 230° and 240° being kept. Gautier¹ gives the boiling point as 232°.

The *p*-chloro-acetophenone, dissolved in glacial acetic acid (about 50 g. in 100 cc.) was treated with one molecule of bromine, the latter being added slowly in order to keep the temperature of the reacting mixture from rising too high. A slow, constant evolution of hydrobromic acid is desirable. The *p*-chlorophenacyl bromide separated in yellow crystals as it was formed.

Upon completion of the bromination the mixture was cooled to 0° and the crystals collected on a filter. To separate them further from any oily material the crystals were centrifuged. The crude product was then dissolved in the least amount of 95% alcohol possible and boiled a few minutes with a mixture of animal and prepared wood charcoal. The saturated solution was then filtered quickly through a hot filter, the *p*-chlorophenacyl bromide separating on cooling as fine, white crystals.

¹ *Ann. chim. phys.*, [6] 14, 373 (1888).

Only one recrystallization of the crude product was necessary to give the pure reagent melting at 96.5° .

The *p*-bromophenacyl bromide was made similarly. Instead of obtaining an oil in the first reaction, however, the *p*-bromo-acetophenone separated as a solid melting at 50.5° . The melting point of this compound, as determined by Schweitzer,¹ is 51° . Upon bromination, as above, *p*-bromophenacyl bromide was obtained as brownish yellow crystals, which required 3 recrystallizations from 95% alcohol before giving fine, white crystals melting constant at 109.7° .

Similar methods were used in the preparation of the *p*-iodophenacyl bromide. There seems to be some doubt in the literature as to the exact melting point of *p*-iodo-acetophenone. Klingel² made this compound from *p*-amido-acetophenone by the diazo-reaction, and obtained a product melting at 79° . Later Schweitzer,³ using the Friedel and Craft reaction, prepared a compound melting at 85° . Schweitzer did not determine the position of groups in his compound, but assumed that, since the analogous method of preparation gave a *p*-chloro- and *p*-bromo-acetophenones, that his product was *p*-iodo acetophenone. The compound obtained in this laboratory was a dark brown mass, which, when centrifuged and recrystallized from 95% alcohol, gave fine, yellow crystals melting at 83.5° . Some of the purified material was dissolved in glacial acetic acid and heated with a slight excess of chromic acid. The oxidation product was precipitated by the addition of water, filtered, washed and dried. It melted at 265° . The dry product was then dissolved in sodium carbonate solution and precipitated by dil. sulfuric acid. The compound again melted at 265° . The melting point of *p*-iodobenzoic acid is given as $265-6^{\circ}$. This shows that the $-\text{COCH}_3$ group enters the *para* position and that the compound is actually *p* iodo-acetophenone.

The *p*-iodo-acetophenone was then brominated, as above. After 5 recrystallizations from 95% alcohol, *p*-iodophenacyl bromide was obtained as fine, slightly yellow crystals melting at 113.5° . Small portions of the product were recrystallized from carbon disulfide, ether and benzene, and in all cases white crystals, turning yellow in the air and melting at 113.5° , were obtained. The *p*-iodophenacyl bromide on analysis gave

Calc.: I, 39.06, Br, 24.59. Found: I, 38.90; Br, 24.57.

The bromination of the halogen acetophenones may be carried out in carbon disulfide also, but much better results are obtained with glacial acetic acid as a medium.

No special attempt was made to obtain the very best yields of final products, the main object being a fairly high degree of purity. The yields

¹ *Ber.*, 24, 550 (1891).

² *Ibid.*, 18, 2692 (1885).

³ *Ibid.*, 24, 551 (1891).

(calculating from the amount of phenyl halide used) of crude products in the case of the *p*-chlorophenacyl bromide were 78-82% (80-85% yield of the *p*-chloro-acetophenone in the first stage and 94-96% of the *p*-chloro-acetophenone converted to *p*-chlorophenacyl bromide in the second stage), of the *p*-bromo compound 70-75% (70-80% yield in the first stage and 90-95% yield in the second stage), and of the *p*-iodo compound 55-60% (50-60% yield in the first stage and 90-95% yield in the second stage).

Method of Work.

The method of preparation of the esters was similar to that used in previous work¹ on the identification of acids. In the case of the *p*-chlorophenacyl esters 0.84 g. of reagent was used, of the *p*-bromo esters one g., and of the *p*-iodo esters 0.58 g., equivalent to 0.5 g. of the *p*-bromo, the smaller quantity being used on account of lower solubility. In a few cases where the degree of solubility of the esters could be predicted, *i. e.*, extremely soluble or difficultly soluble, more or less of the reagent was used as desired. For the addition of solvent, the calculation of the percentage composition of solvent and the filtration and washing of precipitates, the method of procedure adopted by Rather and Reid (*q. v.*), was followed. Monobasic acids were heated on the water bath for one hour, except acetic, propionic, glycolic and lactic which were heated only from $\frac{1}{2}$ to $\frac{3}{4}$ hour, dibasic acids were heated 2 hours and tribasic 3 hours. The precipitation of the esters was brought about by immersion of the flask in tap-water, except in a few cases where it was necessary to cool to 0° in order to start crystallization. The reagents and acids were weighed to 0.01 g. and the alcohol and water measured from pipets. Where it was possible to obtain them the alkali salts of the acids were used, otherwise the free acid was not quite neutralized with sodium carbonate in the reaction flask just before the reagent and alcohol were added. In the case of stearic, palmitic and margaric acids a solution of sodium alcoholate, containing the required amount of base, was added to the acid and warmed until the sodium salt of the acid precipitated on cooling. The reagent and solvent were then added and the ordinary procedure followed.

Recrystallization of the esters was carried out until a constant melting point was obtained. The melting points were taken in a small beaker containing conc. sulfuric acid which was well stirred. The same thermometer was used throughout, no corrections being applied. The thermometer registered correctly at 0° and 0.1° too low at 100°, while the melting point of pure benzoic acid taken under the conditions used was 121.5° as compared with the correct melting point of 121.25°.

¹ THIS JOURNAL, 39, 124, 701 and 1727 (1917); 41, 75 (1919).

The solubilities given for the esters are only approximate. The solubilities in the tables below were determined for the boiling alcoholic solution of the percentage composition expressed under "% Solvent" and for the solution cooled to about 20-25°.

Results.

The results of the investigation are given in the following tables in the form used by Rather and Reid (*q. v.*). Table I contains the *p*-chlorophenacyl esters, Table II the *p*-bromophenacyl esters and Table III the *p*-iodophenacyl esters. The first line represents the original preparation and the following lines each succeeding crystallization. The first crop is the quantity of ester precipitated on cooling the alcoholic solution of the percentage composition stated. The second crop is the quantity of ester held in solution at 20-25° and precipitated by dilution with water.

TABLE I.
p-Chlorophenacyl Esters.

Acids,	Solvent		First crop			Second crop			% yield of ester	Cc. solvent to dissolve 1 g. of ester.	
	%	Cc.	Wt.	M. p.	° C.	Wt.	M. p.	° C.		Hot	Cold.
Acetic CH_3COOH	47	20	0.46	65	6	0.14	62	8	78
	31	30	0.35	66	8	trace	65	280
	31	22	0.26	67	2	trace	66
	31	15	0.20	67.2	trace
Aconitic $\text{C}_6\text{H}_4(\text{COOH})_2$	76	25	0.33	167	4	emulsion			44
	95	50	0.08 ^a	168	8	0.17 ^b	168	8	315	650
	95	50	0.06 ^c	169

^a Portion of 1st 1st dissolved by 50 cc. of 95% EtOH.

^b Portion undissolved.

^c Portion of 6 dissolved by 50 cc. of 95% EtOH.

Benzoic	{	63	60	0.75	118.5	0.15	115	91
$\text{C}_6\text{H}_5\text{COOH}$		57	33	0.71	118.6	0.02	118.6	.	44	870

Another preparation gave a yield of 90% and melted at 118.6°.

Ethyl-glycolic $\text{C}_6\text{H}_5\text{OCH}_2\text{COOH}$	63	15	0.59	94.4	0.20	80	86
	27	35	0.54	94.4	60	700
Succinic $(\text{CH}_2\text{COOH})_2$	86	55	0.12	196	(0.44)	(95.5)	16
	95	60	0.05 ^a	197.5	0.05 ^b	197.2	800	2500

^a Portion of 1st 1st dissolved by 60 cc. of 95% EtOH.

^b Portion undissolved.

Thiocyanic HCNS	{	76	25	0.58	135.2	0.15	124	95.5
		55	24	0.48	135.2	0.05	133.5	41	250
Tricarballic C ₆ H ₃ (COOH) ₃	{	81	35	0.39	124	53
		95	50	0.27 ^a	125.6	0.06 ^b	126	150	800
		95	40	0.25	125.6

^a Portion of 1st 1st dissolved by 50 cc. of 95% EtOH.

^b Portion undissolved.

TABLE II
p-Bromophenacyl Esters.

Acids	Solvent		First crop			Second crop			% yield of ester	Cc. solvent to dissolve 1 g. of ester.	
	%	Cc	Wt.	M	p ° C	Wt.	M	p ° C		Hot	Cold.
Acetic CH_3COOH	60	16	0.55	84	5	0.25	82	5	86.5
	40	14	0.48	85		0.01	82	8	...	27	210
	40	14	0.41	85		0.03	83	8
Aconitic $\text{C}_6\text{H}_5(\text{COOH})_2$	79	36	0.41	184		oil			45
	95	70	0.03 ^a	184		0.28 ^b	186			540	...
	95	50	0.01 ^c	186		0.23 ^d	185	5			...
The ester precipitated almost entirely from the hot solution											
^a Portion dissolved by 70 cc. of 95% EtOH											
^b Portion undissolved											
^c Portion of (b) dissolved by 50 cc. of 95% EtOH											
^d Portion of (b) undissolved.											
Anisic $p\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$	86	55	1.17	152		trace			93.5
	95	80	1.05	152		0.06	152			68	625
Benzoic $\text{C}_6\text{H}_5\text{COOH}$	63	30	0.69	119		0.04	110		85		..
	64	22	0.64	119		0.03	118	2		31	470
Another preparation gave a yield of 92% and melted at 119°.											
Butyric, normal $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	63	18	0.62	63		0.23	60	8	83.5
	61	14	0.48	63	2	0.11	63			22	110
	61	14	0.36	63	2	0.11	62	5			...
Butyric, iso. $(\text{CH}_3)_2\text{CHCOOH}$	63	18	0.72	76	2	0.23	74		93		..
	67	17	0.55	76	8	0.14	75			23	95
	46	25	0.51	76	8	0.01	74				...
Capric $\text{CH}_3(\text{CH}_2)_8\text{COOH}$	76	25	1.12	66		0.05	50		87.5
	80	26	0.99	66			65			23	215
Caproic $\text{CH}_3(\text{CH}_2)_6\text{COOH}$	67	17	0.92	71		0.06	66		88		...
	61	43	0.76	71	6		70	5		46	270
	62	35	0.65	71	6		71				...
Caprylic $\text{CH}_3(\text{CH}_2)_7\text{COOH}$	71	40	0.97	65		0.13	60		90
	63	45	0.87	65	5	0.08	63			46	450
	65	41	0.79	65	5	0.07	64		
Cinnamic $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$	66	100	0.81	146					80
	73	67	0.79	145	6					82	2700
	73	65	0.75	145	6				
Citric $\text{HOOC}_3\text{H}_4(\text{COOH})_2$	87	60	0.38	148		..			40.5
	95	85	0.34	148		..				220	1850
If the solution is cooled too rapidly, the ester separates as a gum.											
Erucic $\text{C}_{21}\text{H}_{41}\text{CH}:(\text{CHCH}_3)_{11}\text{COOH}$	84	54	1.74	61		0.16	51		90.5
	88	44	1.62	61				25	360
Ethyl-glycolic $\text{C}_2\text{H}_5\text{OCH}_2\text{COOH}$	54	35	0.79	104	8	0.14	90		85
	47	28	0.71	104	8			35	360

TABLE II (continued).

Acids.	Solvent		First crop.			Second crop			% yield of ester	Cc. solvent to dissolve 1 g. of ester.	
	%	Cc	Wt.	M	p ° C	Wt.	M	p ° C		Hot.	Cold.
Glycolic OHCH_2COOH	47	20	0.71	134	6	0.09	121		81
	23	40	0.61	133	
	47	20	0.45	136		...	123	5	...	32	125
	47	14	0.36	138	
	47	10	0.31	138	
Hippuric $\text{C}_6\text{H}_5\text{CONHCH}_2\text{COOH}$	76	25	1.06	150		0.15	130		89
	52	45	1.00	151		0.03	151			42	750
	50	42	0.94	151	
Hydrocinnamic $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOH}$	76	25	1.19	104		0.05	102		95	5	...
	67	35	1.14	104		0.07	103	5	...	30	625
	63	18	0.19	112	8	0.58	111		74
i. Lactic $\text{CH}_3\text{CHOHCOOH}$	21	58	0.59	112	
	19	25	0.50	112	8	0.02	112	2	...	42	280
	19	21	0.42	112	8

The 1st 1st and 1st 2nd crops were added, together and dissolved in 58 cc. of 21% alcohol, the 0.59 g. of ester precipitating being called 2nd 1st crop.

Laevulmic $\text{CH}_2\text{CO}(\text{CH}_2)_2\text{COOH}$	63	15	0.74	84		0.24	82		86	5	...
	36	65	0.58	84		0.06	84		...	90	425
	39	50	0.47	84		0.05	84	
Margaric $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$	95	30	1.41	78	2	gum	...		84
	91	52	1.18	78	2	...	76		...	36	225
Palmitic $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$	95	30	1.41	81	5	gum	...		86	5	...
	83	34	1.18	81	5	...	80	8	...	24	150
Phenylacetic $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$	76	25	0.62	88	6	0.22	87		94
	68	18	0.48	89		0.03	86		...	30	130
	76	20	0.26	89		0.17	88	8
Propionic $\text{CH}_3\text{CH}_2\text{COOH}$	63	15	0.56	58	8	0.36	55	5	94
	41	25	0.47	59		0.05	59		...	44	300
	47	20	0.35	59	
Pyromucic $\text{C}_6\text{H}_5\text{OCOOH}$	76	25	0.98	138	5	0.07	115		88
	67	28	0.90	138	5	0.03	138	5	...	28	350
Salicylic $\text{o-OHC}_6\text{H}_4\text{COOH}$	76	25	0.88	140		(0.2)	(101)		73
	67	62	0.85	140		0.01	138		...	70	2700
Sebacic $\text{COOH}(\text{CH}_2)_8\text{COOH}$	76	25	0.90	142		0.18	112		75
	95	80	0.29*	147		0.55 ^b	147		...	230	1350
	95	60	0.26*	147	

* Portion of 1st 1st dissolved by 80 cc. of 95% EtOH.

^b Portion undissolved.

* Portion of * dissolved in 60 cc. of 95% EtOH.

Sorbic $\text{CH}_3(\text{CH}=\text{CH})_3\text{COOH}$	76	25	0.95	129		0.04	128	2	89
	63	45	0.91	129		0.02	128	6	...	47	1200
Stearic $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	95	42	1.30	78		0.15	78		84
	87	65	1.14	78	5	...	78	5	...	50	410

TABLE II (continued).

Acids.	Solvent.		First crop			Second crop			% yield of ester.	Cc. solvent to dissolve 1 g. of ester.	
	%.	Cc.	Wt.	M. p.	° C.	Wt.	M. p.	° C.		Hot.	Cold.
Succinic (CH ₂ COOH) ₂	86	55	0.44	210		(0.29)	(105)		47.5
	95	60	0.01 ^a	211		0.39 ^b	211		1200
	95	60	0.01 ^c	211		0.35 ^d	211	

^a Portion of 1st 1st dissolved by 60 cc. of 95% EtOH.^b Portion undissolved.^c Portion of B dissolved by 60 cc. of 95% EtOH^d Portion of B undissolved.

Thiocyanic HCNS	80	38	0.73	147.5	0.14	132	94
	80	30	0.60	146.5	0.10	145	41	240
	60	32	0.53	146.5	0.05	145

The *p*-chloro- and *p*-bromo-thiocyanates are pale yellowish green in color, the only colored esters obtained.

<i>o</i> -Toluic <i>o</i> -CH ₃ C ₆ H ₄ COOH	76	25	0.51	58	(0.27)	(62.5)	57
	54	35	0.45	56.9	emulsion	68	550
	65	41	0.24	56.9
<i>m</i> -Toluic <i>m</i> -CH ₃ C ₆ H ₄ COOH	71	40	0.75	108	5 emulsion	..	84
	65	32	0.69	108	emulsion	42	500
	65	29	0.65	108	emulsion
<i>p</i> -Toluic <i>p</i> -CH ₃ C ₆ H ₄ COOH	81	35	0.79	153	trace	..	88
	79	60	0.74	153	trace	152.5	..	76	1100
Tricarballic C ₆ H ₃ (COOH) ₃	81	35	0.69	137.6	oil	...	76
	95	105	0.50 ^a	138.2	0.11 ^b	137.8	..	180	1330
	95	90	0.42 ^c	138.2		138

^a Portion of 1st 1st dissolved by 105 cc. of 95% EtOH.^b Portion undissolved.^c Portion of * dissolved by 90 cc. of 95% EtOH.

Valeric, normal.	63	18	0.84	63.6	0.14	58	91
CH ₃ (CH ₂) ₄ COOH	67	21	0.61	63.6	0.20	62.5	25	100
Valeric, iso	66	20	0.51	65	0.39	51.5	84
(CH ₃) ₂ CHCH ₂ COOH	66	20	0.41	67	0.03	59	84
	0.37 g. of 2nd 1st taken and dissolved in 33 cc. of 40% alcohol.								
	40	33	0.33	68	0.01	67	90	90	730
	41	23	0.31	68

Another preparation melted at 68°.

Esters Unsuitable for Identification.

The *p*-bromophenacyl esters of asparaginic, maleic, racemic and tartaric acids were obtained in small quantities, but were very difficultly soluble in boiling 95% alcohol. These esters did not melt, but decomposed on heating and hence are of no value for identification purposes. The *p*-bromophenacyl ester of mucic acid was obtained in a minute quantity, insufficient to recrystallize. It decomposed at 215–225°. It was thought that the *p*-chlorophenacyl esters of the above acids would melt,

TABLE III.
p-Iodophenacyl Esters.

Acids.	Solvent.		First crop.		Second crop.		% yield of ester.	Cc. solvent to dissolve 1 g. of ester.	
	%	Cc.	Wt.	M. p. ° C.	Wt.	M. p. ° C.		Hot.	Cold.
Acetic CH_3COOH	63	30	0.57	113	0.16	110	90
	59	32	0.38	114	0.14	113.2	..	56	170
	59	21	0.26	114	0.09	113.5
Benzoic $\text{C}_6\text{H}_5\text{COOH}$	81	35	0.46	126.5	0.11	123.5	86
	63	30	0.43	126.5	0.02	126	..	65	830
Butyric, normal $\text{CH}_3(\text{CH}_2)_2\text{COOH}$	71	40	0.48	80.8	0.56	78	87
	71	16	0.25	81.2	0.20	80.8	..	33	70
	63	15	0.12	81.4	0.10	81.4
Butyric, iso $(\text{CH}_3)_2\text{CHCOOH}$	63	24	0.75	109	0.11	102.5	95
	64	25	0.62	109.2	0.10	107	..	33	210
Capric $\text{CH}_3(\text{CH}_2)_8\text{COOH}$	76	31	0.63	80	0.03	77	88
	83	24	0.50	80	0.10	79.9	..	37	170
Caproic $\text{CH}_3(\text{CH}_2)_4\text{COOH}$	71	32	0.75	81.4	0.15	78	92
	72	34	0.58	81.5	0.14	80.6	..	45	200
Caprylic $\text{CH}_3(\text{CH}_2)_6\text{COOH}$	71	40	0.53	77	0.07	74	86
	82	22	0.34	76.8	0.15	75	..	41	110
	84	17	0.14	77	0.16	76.8
Erucic $\text{C}_{22}\text{H}_{43}\text{CH}:\text{CH}-$ $(\text{CH}_2)_{10}\text{COOH}$	71	40	1.93	72.6	oil	...	92
	95	54	1.51	73.6	gum	28	130
	95	50	1.40	73.8	0.06	72.5
i. Lactic $\text{CH}_3\text{CHOHCOOH}$	58	26	0.55	138.8	0.18	134.5	81
	53	34	0.34	139.8	0.14	138.2	..	61	160
	51	22	0.24	139.8	0.07	139
Margaric $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	95	30	0.61	89	gum	...	66
	95	30	0.48	88.8	trace	88.8	..	49	230
Palmitic $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	95	30	0.69	90	gum	...	77
	90	21	0.66	90	trace	30	800
Propionic $\text{CH}_3\text{CH}_2\text{COOH}$	56	44	0.83	94.6	0.21	91	91
	67	17	0.61	94.9	0.18	93.6	..	20	75
	63	15	0.44	94.9	0.14	94.2
Stearic $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	95	30	0.79	90.8	0.09	74	93
	91	26	0.77	90.5	trace	32	930
Valeric, normal $\text{CH}_3(\text{CH}_2)_3\text{COOH}$	71	20	0.43	76	0.11	72	87
	68	18	0.31	78.6	0.10	75	..	41	145
	68	14	0.22	78.6	0.07	77.9
Valeric, iso $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$	68	28	1.00	72	0.23	69.8	99
	63	30	0.75	78.8	0.20	71	..	30	120
	63	22	0.64	78.8	trace	71

Another preparation of normal valerate gave a yield of 92% and melted at 78.6°.

but the ester of asparaginic decomposed at 145–150° and that of racemic decomposed at 180–190°. It was, therefore, not considered worth while to try tartaric, maleic or mucic acids. The data in regard to the *p*-bromophenacyl esters of asparaginic, maleic, racemic and tartaric acids is given in Table IV.

TABLE IV
p-Bromophenacyl Esters

Acids	Solvent	First		Temp of decomp °C	Second		Temp of decomp °C	% yield of ester	Cc solvent to dissolve 1 g of ester	
									Hot	Cold
Asparaginic $\text{NH}_2\text{CO}(\text{NH})_2\text{C}_3\text{H}_5\text{COOH}$	83	40	o 26	140–50	oil	...	22
	95	70	AO 02	175–6	Bo 11	170	..	470
Maleic $\text{HOOCCH} : \text{CHCOOH}$	80	36	o 24	190	(o 41)	(100)	27
	95	60	AO 03	168–70	Bo 10	225–30	..	420	900	...
Racemic (OHCHCOOH)	71	40	o 47	204–6	(o 16)	(108 8)	48
	95	70	AO 11	204–6	Bo 32	205	..	460	1600	...
Tartaric (OHCHCOOH)	71	40	o 56	170	(o 16)	(109)	57
	95	60	AO 04	210–15	Bo 44	215–6	..	490

In all the above cases A is portion of 1st 1st dissolved by 95% EtOH and B is the portion undissolved.

Acids Giving Negative Results.

These acids were tried with the *p*-bromo- and *p*-iodophenacyl bromides. Gallic acid gave a precipitate only in extremely dilute alcohol solutions. This was unsatisfactory as it was finely divided and difficult to filter and dry. It decomposed at 175–190° without a definite melting point.

The sodium salt of linoleic acid seemed to react with the reagents to a small extent only and the precipitates obtained with both reagents were saturated with an oil which could not be entirely removed. The melting points of both esters were about the same and kept slowly rising with each recrystallization, running from 66° to 78°.

Oleic acid behaved similarly with both reagents, the melting points of the supposed esters running from 53° to 63°.

It is possible that the small precipitate formed was the ester of some other fatty acid present as an impurity in the linoleic and oleic acids, and from which they could not be separated.

Oxalic, monochloro-acetic and trichloro-acetic acids did not react at all as the pure reagent was obtained from the solutions nearly quantitatively.

Formic acid in 2 cases did not react as the reagent was recovered pure. In one case a small amount of a precipitate was obtained, before the reagent separated, which softened and melted at 115–9°. Not enough of this was obtained with which to work, and further attempts gave none at all.

The only acid to give a liquid ester was α -oxybutyric. This was tried with both the *p*-bromo- and *p*-iodophenacyl bromides, but in both cases the esters remained oils at 0°.

Analysis of Esters.

Several esters were chosen at random and analyzed. The results are as follows:

Ester	Analysis for	Calc %	Found %
<i>p</i> -Bromophenacyl- <i>m</i> -toluate-Br		24.00	24.23
<i>p</i> -Bromophenacyl thiocyanate-Br		31.20	31.42
<i>p</i> -Chlorophenacyl benzoate Cl		12.91	13.10
<i>p</i> -Bromophenacyl benzoate Br		25.04	25.14
<i>p</i> -Iodophenacyl benzoate-I		34.66	34.88
<i>p</i> -Iodophenacyl norm. valerate I		36.66	36.57

This seemed to indicate that the reagents were reacting in the way expected.

Comparison of *p*-Halogen Phenacyl Esters with Phenacyl and *p*-Nitrobenzyl Esters.

As can be seen, by comparing Tables I, II and III, the yields of *p*-chlorophenacyl esters are slightly lower than the yields of corresponding *p*-bromophenyl esters, and those of the *p*-bromo are lower than those of the *p*-iodophenacyl esters. The same relation holds for the melting points although the difference is more marked than in the case of the yields, the melting points of the *p*-chloro esters running about 10° lower than those of the *p*-bromo esters, and those of the *p*-bromo esters about 10° lower than those of the *p* iodo esters.

For general purposes the *p*-bromophenacyl esters are more useful for identification than the *p*-chloro- or *p*-iodophenacyl esters. On comparing 18 of the *p*-bromophenacyl esters with the corresponding *p*-nitrobenzyl esters the yields in both cases average 80%, while the average melting point of the *p*-nitrobenzyl esters is 84.1° and of the *p*-bromophenacyl esters is 118.8°, giving 34.7° in favor of the latter.

Comparing the *p*-bromophenacyl esters with the corresponding phenacyl esters it is seen that although the average yield of the former is only 70% while that of the latter is 82%, the average melting point of the former is 130.7° against only 96.3° for the phenacyl esters.

In every case the *p*-bromophenacyl ester melted higher than the corresponding *p*-nitrobenzyl or phenacyl esters.

A further comparison of the value of the reagents shows that phenacyl bromide is particularly good in the case of the dibasic acids. *p*-Bromophenacyl bromide gave very poor results with dibasic acids, but for monobasic acids, especially those of the formic acid series, it gave better results than any other reagents thus far tried.

p-Halogen Phenacyl Alcohols.

Since the *p*-halogen phenacyl esters are derivatives of the corresponding alcohols, it was considered to be a matter of interest to prepare the latter. The method of preparation was similar to that used by O. Fischer¹ for benzoyl carbinol, and recommended by Straus for the *p*-chlorophenacyl alcohol, *i. e.*, the hydrolysis of the *p*-halogen phenacyl acetates in water containing a slight excess of barium carbonate. The following proportions of materials were used with good results: 2 g. of *p*-chlorophenacyl acetate, one g. of barium carbonate and 100 cc. of water; 2 g. of *p*-bromo-acetate, 0.8 g. of barium carbonate and 125 cc. of water; and 2 g. of *p*-iodoacetate, 0.7 g. of barium carbonate and 150 cc. of water. The acetate was put in an Erlenmeyer flask with the required amount of barium carbonate and water and refluxed for about one hour. The solution was filtered hot, the alcohol crystallizing out, upon cooling, in fine, white plates. The *p*-chlorophenacyl alcohol melted at 122.4°, when crystallized from water, ether and absolute alcohol, which checks well with Straus' observation of 122-3°. *p*-Bromophenacyl alcohol melted at 136.6° and *p*-iodophenacyl alcohol melted at 152°. The alcohols are very soluble in ether, hot water and hot alcohol, crystallizing well from the latter. Analyses of the *p*-bromo and *p*-iodo alcohols gave the following results:

Calc. for *p*-bromophenacyl alcohol Br, 37.16. Found: 36.98.

Calc. for *p*-iodophenacyl alcohol I, 48.43. Found: 48.24.

The analyses and melting points (crystallization from water, ether and alcohol giving identical melting points) also indicate that the alcohols contain no water of crystallization. No analysis of the *p*-chlorophenacyl alcohol was made, as it was evident that it was identical with the compound prepared by Straus, who analyzed his product.

Summary.

The *p*-halogen phenacyl bromides, particularly *p*-bromophenacyl bromide, serve as useful reagents for the identification of acids, especially monobasic aliphatic acids. They are easily prepared and react readily with the alkali salts of the acids when boiled in dil. alcohol solutions. The range of the melting points of the esters is very convenient for identification purposes.

The following esters have been prepared and studied:

<i>p</i> -Chlorophenacyl Esters.			
	M. p. °C.		M. p. °C.
Acetate.....	67.2	Succinate	197.5
Acrylate.....	169.0	Thiocyanate.....	135.2
Benzoate.....	118.6	Tricarballoylate.....	135.6
Ethyl-glycolate.....	94.4		

¹ Ber., 24, 2680 (1891).

<i>p</i> -Bromophenacyl Esters			
	M	P °C	M P °C.
Acetate	85	0	84 0
Aconitate	186	0	78 2
Anisate	152	0	81.5
Benzoate	119	0	89 0
Butyrate	63	2	59 0
Iso-butyrate	76	8	138 5
Caprate	66	0	140 0
Caproate	71	6	147 0
Caprylate	65	5	129 0
Cinnamate	145	6	78 5
Citrate	148	0	211 0
Erucate	61	0	146 5
Ethyl-glycolate	104	8	56 9
Glycolate	118	0	108 0
Hippurate	151	0	153 0
Hydrocinnamate	104	0	138 2
Lactate	112	8	63 6
		Isovalerate	68 0

<i>p</i> -Iodophenacyl Esters.			
	M	P °C	M P °C.
Acetate	114	0	73 8
Benzoate	126	5	139 8
Butyrate	81	4	88 8
Iso butyrate	109	2	90 0
Caprate	80	0	94 9
Caproate	81	5	90 5
Caprylate	77	0	78 6
Iso-valerate	78	8	

BALTIMORE, MARYLAND

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE]
THE ADDITION OF 1,3-DIKETONES TO ISOTHIOCYANATES.
I. ACETYLACETONE AND CERTAIN ARYL
ISOTHIOCYANATES.

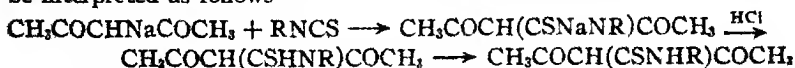
BY DAVID E. WORRALL

Received March 1, 1920

The β -diketones are characterized by several reactions that make them of particular value for synthetic purposes. They react with hydroxylamine and with phenylhydrazine to form mono-substituted derivatives; but, through the loss of a molecule of water, these rearrange to form isoxazols and pyrazols, reactions that illustrate the ease with which 5-membered ring compounds may be closed. The presence of an acidic methylene group makes possible the formation of metal derivatives; hence these diketones are capable of transformations similar to those so well known with malonic ester.

Phenyl mustard oil reacts readily with sodium acetoacetic and malonic esters to form thio-anilides.¹ This reaction was shown later to be general for aryl mustard oils.² It has now been found that the addition takes place just as readily with the sodium derivative of 1,3-diketones and probably is a general reaction for similar compounds containing hydrogen replaceable by a metal. This will be investigated in order to find the scope and limits of the reaction. Work is in progress with other diketones and esters.

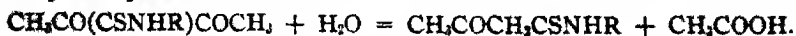
Sodium acetylacetone was found to react at room temperature with phenyl-, with the 3 tolyl- and with *p*-bromophenyl isocyanates. The final product in each case was a thio-anilide. The transformations may be interpreted as follows



The derivatives of phenyl isothiocyanate in which the substituents were in the *para* position were found to be slightly more reactive with sodium acetylacetone than phenyl iso-thiocyanate. The nature of the substituent in the 2 cases investigated was of little, if any significance, since *p*-bromo- and *p*-methylphenyl-isothiocyanates were added to sodium acetylacetone with equal ease, as near as could be judged. The position of the substituent, however, was of decided influence and both *o*- and *m*-tolyl-isothiocyanates reacted much more slowly with the diketone.

Finely divided metallic sodium was used to prepare sodium acetylacetone, in order to avoid the use of alcohol because of the possibility of urethane formation with the isothiocyanate. A varying but small amount of unchanged sodium was always present before the addition of water. While this undoubtedly cut down the yield somewhat it had no other effect. In favorable cases the yield of crude product was about 80% of the calculated amount, occasionally much less, of which 20% was lost in purifying the substance by recrystallization.

The resulting thio-anilides dissolved easily in dil. caustic alkali solution and, on neutralization with acid, new substances, the result of hydrolysis, separated,



The 2 series of anilides reacted very readily with organic bases such as phenylhydrazine and hydroxylamine; the point of attack was the sulfur atom. The same product was formed from the 2 corresponding anilides in each case. Thus thio-diaceto-acetyl anilide and thio-aceto-acetyl anilide gave rise to the same substance with phenylhydrazine, namely

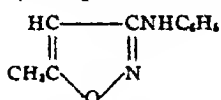
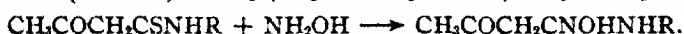
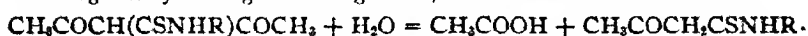
¹ Michael, *J. prakt. Chem.*, [2] 35, 450 (1887), [2] 60, 286 (1889); Ruheman, *J. Chem. Soc.*, 93, 621 (1908).

² Worrall, *THIS JOURNAL*, 40, 415 (1918).

the hydrazone of thioformanilide. Reduction as well as condensation must have taken place.



The action of hydroxylamine appeared to result in the formation of an isoxazol. Thio-diaceto-acetyl anilide and thio-aceto-acetyl anilide formed the same product, showing the ease with which the former is hydrolyzed. The resulting anilide then condensed with hydroxylamine, with the elimination of hydrogen sulfide. Reduction did not take place in this case and as the resulting oxime contained a carbonyl group in the β -position to the oxime radical, conditions were favorable for anhydride formation, resulting finally through rearrangement, in an isoxazol.



This compound is insoluble in alkali, soluble in conc. hydrochloric acid, in which it is unchanged by short heating, and does not appear to react with acetyl chloride.

Experimental.

Thio-diaceto-acetyl Anilide, $\text{CH}_3\text{COCH}(\text{CSNHC}_6\text{H}_5)\text{COCH}_3$.—Ten g. of acetylacetone was converted into the sodium derivative by addition to 2.3 g. of sodium suspended in 100 cc. of ether. A vigorous reaction took place at first, but was not completed for some time. Accordingly, the mixture was kept at room temperature for at least 24 hours before it was used. The molecular equivalent of phenyl-isothiocyanate was added. The ether became colored yellow in a few minutes, while the white powdery sodium acetylacetone slowly changed into a heavy yellow granular solid, somewhat pasty when it separated out on the sides of the container. After several days the mixture was treated with ice-water, the water layer separated and poured into a large volume of cold dil. hydrochloric acid. The turbid solution deposited a voluminous crystalline precipitate in a few minutes. This was separated, crystallized twice from benzene and air-dried at 100° .

Calc. for $\text{C}_{15}\text{H}_{14}\text{ONS}$: N, 6.0; S, 13.6. Found: N, 6.8; S, 13.4.

The sulfur was determined by treating a weighed amount of the substance with an excess of phenylhydrazine. The mixture was warmed gently to complete the reaction. The hydrogen sulfide evolved in an atmosphere of hydrogen was forced to bubble through ammoniacal cadmium sulfate solution and the resulting cadmium sulfide was separated and heated to constant weight at 110° in a Gooch crucible. This pro-

cedure was necessary, as it was found to be extremely difficult to oxidize this thio-anilide completely with nitric acid. A vigorous reaction took place at room temperature, but the resulting yellow substance was not entirely decomposed after 3 hours heating in a sealed tube at 200–250°. This compound was not identified, but was found to be free from nitrogen, although it contained sulfur. This work with nitric acid was done by Mr Lee Smith, of Harvard University, in attempts to determine sulfur by the Carius method.

Thio-diaceto-acetyl anilide is readily soluble in alcohol, acetone, ammonium hydroxide and conc. acids. It is less soluble in benzene and insoluble in petroleum ether and water. It crystallizes from benzene in slender pale yellow needles, which melt at 107–108°. It is unstable toward alkaline reagents more stable with the mineral acids, but easily decomposed by the latter if heated. Bromine is readily absorbed with subsequent evolution of hydrogen bromide.

The thio-anilide is completely decomposed by hot hydrochloric acid. Hydrogen sulfide is evolved, acetic acid formed, and also aniline hydrochloride. Potassium permanganate is easily reduced in the cold with the formation of isonitrile, recognized by its characteristic odor.

Thio-aceto-acetyl Anilide, $\text{CH}_3\text{COCH}_2\text{CSNHC}_6\text{H}_5$.—Two g. of thio-diaceto-acetyl anilide was dissolved in dil. potassium hydroxide solution and kept at room temperature for a few hours. It was then cooled with ice and cautiously neutralized with cold dil hydrochloric acid. A pale yellow oil separated. It quickly hardened to a crystalline mass and was recrystallized from alcohol diluted with water.

Calc. for $\text{C}_{10}\text{H}_{11}\text{ONS}$: N, 7.3 Found 7.8

It is very soluble in alcohol, benzene, ether, etc., and sparingly soluble in hot water. It is easily superfused, so the following procedure was devised as most convenient for purification. The crude product is dissolved in hot alcohol and warm water is added until a faint turbidity appears. The mixture is allowed to cool to room temperature, filtered to remove tarry material that forms, and then placed in a cold place overnight. The thioaceto-acetyl anilide separates in brilliant yellow plates, m. p. 63.5–64°. The reactions of this substance are very similar to those of the diaceto derivative, due to the ease with which the latter hydrolyzes to form acetic acid and thio-aceto-acetyl anilide.

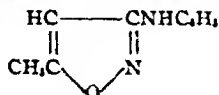
Action of Phenylhydrazine on Thio-diaceto-acetyl Anilide.

Two g. of anilide was mixed with the molecular equivalent of phenylhydrazine. The mixture quickly became warm with an immediate evolution of hydrogen sulfide. It was heated for an hour on the steam bath and then cooled. The resulting oil hardened on standing to a stiff paste which was pressed on a clay plate and crystallized twice from benzene.

Calc. for $C_{15}H_{13}N_3$: N, 19.9. Found: 20.2.

The new substance is the phenylhydrazone of thioformanilide, $HC(NNHC_6H_5)NHC_6H_5$. It separates from benzene-petroleum ether mixture in lustrous white plates, which are somewhat irregular, m. p. 126–127°. It may be crystallized from water. If heated for a few minutes with conc. hydrochloric acid, crystals of phenylhydrazine hydrochloride separate. These were identified by the melting point, 240°, and by treating the salt neutralized with sodium hydroxide with benzaldehyde. The oil first formed quickly reacted to form a crystalline derivative.

3-Anilino-5-methylisoxazol.—Three g. of thio-diaceto-acetyl anilide,



dissolved in alcohol, was refluxed for several hours with free hydroxylamine, prepared by neutralization of the hydrochloride with potassium carbonate. The colorless solution was then evaporated to a small volume, the precipitate crystallized from hot water and dried *in vacuo*.

Calc. for $C_{15}H_{15}ON_2$. N, 16.1. Found: 16.5.

It is soluble in the usual organic solvents except petroleum ether and may be crystallized from benzene, or a large volume of water, in slender colorless needles melting at 111–112°. It is insoluble in cold alkali, but somewhat soluble in hot sodium hydroxide solution, from which it subsequently separates unchanged. It is not decomposed by short heating with conc. hydrochloric acid, in which it is easily soluble.

Thio-diaceto-acetyl *p*-Toluide, $\text{CH}_3\text{COCH}(\text{CSNHC}_6\text{H}_4\text{CH}_3)\text{COCH}_3$.—Five g. of acetylacetone was converted into the sodium derivative and mixed with the molecular equivalent of *p*-tolyl mustard oil. At the end of 3 days the mixture was dissolved in cold water, the water layer separated and acidified with cold dil. acid. The yield was slightly over 10 g. of crude material from which 8 g. of pure substance was recovered by crystallization from benzene.

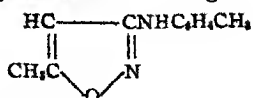
Calc. for $C_{24}H_{21}O_2NS$: N, 5.6. Found: 6.4.

The thiotoluide crystallizes from benzene in balls of pointed yellow plates that melt at 132–133°.

Thio-aceto-acetyl-*p*-Toluide, $\text{CH}_3\text{COCH}_2\text{CSNHC}_6\text{H}_4\text{CH}_3$.—Two g. of thio-aceto-acetyl-*p*-toluide was dissolved in a warm solution of potassium hydroxide. After a few hours the solution was neutralized with acid. The precipitate which formed was recrystallized from dil. alcohol as pale yellow microscopic needles, melting at 68–69°.

Calc. for $C_{17}H_{15}ONS$: N, 6.8. Found: 7.2.

3-*p*-Toluidino-5-methylisoxazol.—Two g. of thio-diaceto-acetyl-*p*-



toluide was dissolved in alcohol and refluxed with the molecular equivalent of free hydroxylamine until the evolution of hydrogen sulfide ceased. The alcohol solution was evaporated to a small volume and the product which separated on cooling was crystallized from benzene. Petroleum ether was then added to complete the separation of the glistening white needles, m. p. 122–124°.

Calc. for $\text{C}_{11}\text{H}_{13}\text{ON}_2$: N, 14.9 Found 15.2.

Thio-aceto-acetyl-*p*-bromoanilide, $\text{CH}_3\text{COCH}(\text{CSNHC}_6\text{H}_4\text{Br})\text{COCH}_3$.—Five g. of the diketone was changed to the sodium compound to which the molecular equivalent of *p*-bromophenyl mustard oil was added. After several days the new compound was separated in the usual way. The product was purified by crystallization from benzene to which petroleum ether was added to complete the separation. The ball-like aggregate of tiny flattened needles separating out was filtered and dried. The yield of pure substance was about 9 g., m. p. 137–139°.

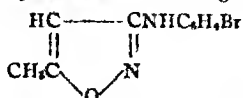
Calc. for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}_2\text{Br}$: N, 4.5 Found 5.1.

The original preparation contained a small amount of a high-melting derivative. This separated on the addition of water and was not further examined at the time.

Thio-aceto-acetyl-*p*-bromoanilide, $\text{CH}_3\text{COCH}_2\text{CSNHC}_6\text{H}_4\text{Br}$.—A small amount of the diaceto-anilide was dissolved in a warm solution of potassium hydroxide, kept at room temperature for a day and then neutralized with acid. The product was recrystallized from dil. alcohol and melted at 110–111°.

Calc. for $\text{C}_{11}\text{H}_{10}\text{ONSBr}$: N, 5.1 Found 5.5.

3-*p*-Bromoanilino-5-methylisoxazol.—Two g. of the original bromo



derivative was refluxed with the molecular equivalent of hydroxylamine until no further action ensued. The filtered solution on standing deposited crystals which were recrystallized from alcohol. The resulting slender, nearly colorless, needles melted at 178–180° with preliminary darkening of color.

Calc. for $\text{C}_{10}\text{H}_9\text{ON}_2\text{Br}$: N, 11.2. Found: 11.5.

Thio-diaceto-acetyl-*m*-toluide, $\text{CH}_3\text{COCH}(\text{CSNHC}_6\text{H}_4\text{CH}_3)\text{COCH}_3$.—Three g. of *m*-tolyl isothiocyanate was added to the molecular equivalent

of sodium acetylacetone and allowed to stand for a week. The new sodium derivative was dissolved in ice-water and decomposed with cold dil. acid. A vivid yellow oil separated and slowly hardened on standing. Only about a gram of the product was obtained. It crystallized from benzene mixture in shining yellow plates, m. p. 124-125°.

Calc. for $C_{14}H_{12}O_4NS$: N, 5.6. Found. 6.1.

Thio-diaceto-acetyl-*o*-toluide, $CH_3COCH(CSNHC_6H_4CH_3)COCH_3$.—Five g. of acetylacetone was converted into the sodium derivative and kept for a week with the equivalent of *o*-tolyl isothiocyanate mixed with ether. The mixture treated in the customary manner, gave 3 g. of crude material. This was purified by use of benzene-petroleum ether. Pale yellow irregular plates were obtained, m. p. 126.5-128°.

Calc. for $C_{20}H_{18}O_4NS$: N, 5.6. Found 6.1.

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[CONTRIBUTION FROM THE OFFICE OF PLANT PHYSIOLOGICAL AND FERMENTATION INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

THE MOSAIC DISEASE OF SPINACH AS CHARACTERIZED BY ITS NITROGEN CONSTITUENTS.¹

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Introduction.

Spinach belongs to leafy vegetables which are essentially different from what may be classed as seeds, roots, and tubers. While the latter² representing storage organs contain chiefly reserve proteins, carbohydrates and fats, and but very little active protoplasm, the former³ are made up of a large quantity of functioning cells combined with reserve food material. Whereas roots,⁴ seeds and tubers are deficient in certain inorganic elements and in the dietary essential, fat soluble vitamine A, containing at the same time proteins of low biological value, leaves are comparatively rich in inorganic elements, especially in calcium and sodium, as well as in the fat-soluble vitamine A. This is especially true of spinach⁵ (*Spinacia oleracea*), which is comparatively rich both in the fat-soluble vitamine A and in the water-soluble vitamine B, being twice as efficient as whole wheat, soy beans, dried eggs or milk solids. These important nutritive qualities of spinach make it desirable to ascertain the nature of the mosaic disease of spinach with the object in view of finding a proper remedy for the disease.

¹ Presented before the Division of Biological Chemistry at the St. Louis meeting of the American Chemical Society, April 12-17, 1920.

² McCollum, Simmonds and Parsons, *J. Biol. Chem.*, 38, 115 (1919).

³ McCollum, Simmonds and Pitz, *ibid.*, 30, 19 (1917).

⁴ *Loc. cit.*

⁵ Osborne and Mendel, *ibid.*, 37, 190 (1919).

Briefly stated, the mosaic disease of spinach, widely known as "spinach-blight," is characterized by a few well-defined symptoms. While the leaves of normal spinach plants have a uniform deep-green color, those of blighted plants show a rather yellowish green color, especially between the veins being at the same time mottled and malformed. Whereas the roots of healthy plants are well developed, those of diseased plants are characterized by their shrunken appearance and a loss of lateral rootlets. Generally speaking, the blighted plants show considerable dwarfing, so that the effect of the disease¹ may be said to be a material reduction of the crop (up to 20%) and a lowering of its quality.

In previous papers it was demonstrated that the disease is not due to the inability of the blighted plants to produce carbohydrates,² as is evident from the fact that leaves of diseased spinach have even a larger proportion of carbohydrates than those of normal plants, there being no marked difference in the diastatic activities of blighted and healthy plants. It was further shown that spinach plants affected with the mosaic disease have a lower ash³ content (in the tops) but a higher oxidase⁴ content than do normal plants. While the above data are of considerable value and interest, they failed to reveal the nature of the spinach disease. It was with the hope of attaining this object that a study of the nitrogen metabolism⁵ in the spinach plant was undertaken in 1915. This study has led, among other things, to the assumption that denitrification takes place in the diseased plants, it being based largely on the facts that the diseased plants have been found to contain less total and acid amide nitrogen but more ammoniacal nitrogen than the normal plants. The results, however, may have been incidental to the particular spinach samples of that season. Hence, it seemed important, if not imperative, to corroborate those results by observations on spinach samples taken from various other fields and at other seasons. This was also prompted by the consideration that the disease in question assumes greater significance in view of the fact that a disease similar to or identical with spinach blight has been found to affect several other plants of vast economic importance.

Now if denitrification takes place in diseased spinach we should naturally expect less nitrates in blighted plants than in normal, while nitrites, if present at all, would be expected in the former rather than in the latter. Moreover, in the case of proteins hydrolyzed and separated according to Hausmann's method, the phosphotungstic acid precipitate and the filtrate from it consist of diamino and monoamino acids, respectively.

¹ A complete description of the disease is given by McClintock and Smith, *J. Agr. Research*, 14, 2 (1918).

² True and Hawkins, *ibid.*, 15, 381 (1918).

³ True, Black and Kelly, *ibid.*, 15, 372 (1918).

⁴ *Ibid.*, 15, 377 (1918).

⁵ Jodidi, Kellogg and True, *ibid.*, 15, 385 (1918).

This, however, may not necessarily hold good for spinach, since plants are known to contain, in addition to amino acids and acid amides, also nuclein bases, purin bodies, alkaloids, etc. For this reason it was of considerable moment to find out just what proportion of the basic and non-basic nitrogen as represented by the phosphotungstic acid precipitate and its filtrate is actually made up of diamino and monoamino acids, respectively. This work, too, suggested itself for the reason that while amino acids are known to have nutritive value, it is doubtful whether other nitrogenous compounds, such as acid amides, ammonia, etc., play any role in nutrition.

Experimental.

The spinach samples, both healthy and diseased, used in this work were taken in April, 1918, from beds on the Childreth farm at Lenox, Va.¹ They were separately dried first at room temperature for several days, to be then subjected to the temperature of about 50° for 1 to 2 days in an electric drying oven in which slight vacuum was maintained. The dried materials were then powdered, passed through a 40-mesh sieve and put into sealed jars, ready for use.

Methods.—The *total nitrogen* of the spinach materials was estimated according to the Gunning modification of Kjeldahl's method.

The *nitric nitrogen* was determined as follows. A definite amount of the spinach material was repeatedly extracted with alcohol (85%), the combined extracts made alkaline with milk of lime and evaporated to dryness at low temperature. The residue was taken up with hot water, treated with lead acetate solution, and finally made up to 1000 cc. Of the perfectly clear filtrate aliquot portions, usually 400 cc., were concentrated to about 50 cc., and their nitric acid content determined according to Schulze-Tiemann's² method.

The estimation of *ammonia* was carried out according to Grafe's³ method, whereby the finely powdered materials are treated with a saturated solution of sodium carbonate mixed with sodium chloride solution, and the ammonia thus set free is distilled off *in vacuo* at a temperature ranging from 25 to 37°. Alcohol is usually added to prevent foaming.

As to nitrous acid the spinach materials were examined only qualitatively.

Protein nitrogen was determined according to Stutzer's⁴ method, whereby the protein is precipitated essentially by means of a glycerol-copper

¹ The authors wish to express their appreciation to Prof. T. C. Johnson, Director, Va. Truck Expt. Station, and to Mr. J. B. Norton, Office of Cotton, Truck and Forage-Crop Disease Investigations, for valuable assistance in securing the spinach samples.

² Abderhalden's "Handbuch biochem. Arbeitsmeth.," 6, 312 (1912).

³ Z. physiol. Chem., 48, 300 (1906).

⁴ J. Landw., 28, 105 (1880); 29, 475 (1881); Z. physiol. Chem., 6, 373 (1882).

hydroxide suspension, the precipitate obtained being oxidized according to the Kjeldahl method.

The separation of the *non-protein* nitrogen into the various groups was carried out according to Hausmann's method whereby one g. of magnesium oxide was used for distilling off the acid amide¹ nitrogen. Other methods used in this work will be described subsequently.

The results secured are summarized in the following tables:

TABLE I.—PERCENTAGE OF NITROGEN IN THE OVEN-DRIED SPINACH.

Healthy spinach material.	Nitrogen found. %.	Blighted spinach material.	Nitrogen found. %.	Difference in nitrogen content. %.
Leaves (Sample A)	4.98	Leaves (Sample A)	3.89	—21.89
Leaves (Sample A)	4.98	Leaves (Sample A)	3.83	—23.09
Leaves (Sample A)	5.03	Leaves (Sample A)	3.92	—22.06
Leaves (Sample B)	4.90	Leaves (Sample B)	3.79	—22.65
Leaves (Sample B)	4.82	Leaves (Sample B)	3.80	—21.16
Leaves (Sample B)	4.90	Leaves (Sample B)	3.80	—22.45
Roots	3.90	Roots	3.95	+1.28
Roots	3.90	Roots	3.92	+0.51
Roots	3.94	Roots	3.88	—1.52
....			3.89

Discussion.

By reference to Table I it will be seen that, under normal conditions, the proportion of nitrogen in the leaves is considerably higher (up to 25%) than in the roots, while the nitrogen content of blighted leaves and roots is about the same. Further, it will be noticed that the nitrogen content of the leaves, which constitute the bulk of the plant, is very much lower in the diseased plants than in the healthy ones, the difference ranging from 21.16 to 23.09%, while the difference in the nitrogen content of the diseased and healthy roots is so small as to be negligible. It may be mentioned here that similar results were obtained with spinach samples of the season 1915-1916,² the diseased leaves and the plants as a whole showing in *all instances* a considerably lower nitrogen content than the normal ones, so that the *lower nitrogen content of the diseased tissues may safely be considered as one of the striking characteristics of the mosaic disease of spinach.*

Examination of Table II reveals the fact that the leaves of the healthy spinach have normally a somewhat higher nitric nitrogen content than the roots, the reverse being true of the blighted spinach. The chief difference, however, lies in the tops, the healthy leaves being very much richer in nitric nitrogen (up to 50%) than the diseased, while the difference in the nitrate content of the healthy and blighted roots is but slight. Inasmuch as the distinctions noticed hold good for *all samples and seasons*

¹ Jodidi and Moulton, *THIS JOURNAL*, 41, 1526 (1919).

² Jodidi, Kellogg and True, *J. Agr. Research*, 15, 390 (1918).

TABLE II.—PERCENTAGE OF NITRIC NITROGEN IN THE SPINACH (SEASON 1918).

Healthy spinach material.	Nitric nitrogen			Diseased spinach material	Nitric nitrogen.		
	Soluble nitrogen. %.	Oven-dried spinach %	Total nitrogen. %		Soluble nitrogen. %	Oven-dried spinach. %.	Total nitrogen. %.
Leaves (Sample 1)	6.87	0.17	3.42	Leaves (Sample 1)	4.65	0.08	2.20
Leaves (Sample 1)	6.89	0.17	3.43	Leaves (Sample 1)	4.65	0.08	2.20
Leaves (Sample 2)	7.69	0.19	3.83	Leaves (Sample 2)	5.97	0.11	2.82
Leaves (Sample 2)	8.07	0.19	4.02	Leaves (Sample 2)	5.84	0.11	2.76
Roots	6.30	0.13	3.30	Roots	. .	0.12	3.01
				Roots	.	0.12	3.02

PERCENTAGE OF NITRIC NITROGEN IN THE SPINACH (SEASONS 1915 AND 1916).*

Leaves	6.62	0.17	3.36	Leaves	2.64	0.06	1.39
Leaves	6.86	0.18	3.48	Leaves	2.62	0.06	1.38
Leaves	6.80	0.18	3.45	Entire plant	3.06	0.06	1.60
Entire plant	7.41	0.19	3.92	Entire plant	3.02	0.06	1.58
Entire plant	7.31	0.19	3.87	Entire plant	2.96	0.05	1.55

* It goes without saying that the nitric nitrogen estimations of the spinach materials for the seasons 1915 and 1916 have not been published yet.

examined the conclusion seems to be justified that a *lower nitrate content of the blighted tissues is another striking characteristic of the mosaic disease of spinach.*

TABLE III.—PROPORTION OF NITROUS AND AMMONIACAL NITROGEN IN THE SPINACH.

Healthy spinach material.	Nitrites %	Ammoniacal nitrogen			Diseased spinach material	Nitrites %	Ammoniacal nitrogen		
		Soluble nitrogen %	Oven-dried spinach %	Total nitrogen %			Soluble nitrogen %	Oven-dried spinach. %.	Total nitrogen %.
Leaves	0.0	3.80	0.092	1.89	Leaves	Present	5.40	0.097	2.55
Leaves	0.0	3.80	0.092	1.89	Leaves	Present	5.40	0.097	2.55
Leaves	0.0	4.02	0.097	2.00					
Roots	0.0	5.12	0.105	2.68	Roots		5.80	0.094	2.41
Roots	0.0	5.04	0.103	2.64	Roots		5.80	0.094	2.41

Inspection of Table III shows that the proportion of ammoniacal nitrogen in the diseased leaves is higher than in the healthy, the difference in the ammonia content of the roots of diseased and normal plants being insignificant, and while nitrites are present in diseased tissues none could be detected in normal ones. Hence, *higher ammonia content and presence of nitrites may be said also to be characteristic of spinach blight.*

The importance of proteins as carriers of life in the plant organism and their significance in nutrition suggested the estimation of protein nitrogen in the various spinach tissues. A glance at Table IV shows that in the normal plants the proportion of protein and protein nitrogen is higher in the leaves than in the roots when calculated on the oven-dried

TABLE IV.—PROPORTION OF PROTEIN IN THE SPINACH.

	Protein nitrogen.			Corresponding protein.			Protein nitrogen.			Corresponding protein.	
	Fresh spinach %.	Oven-dried spinach %.	Total nitrogen %.	Fresh spinach %.	Oven-dried spinach %.		Fresh spinach %.	Oven-dried spinach %.	Total nitrogen %.	Fresh spinach %.	Oven-dried spinach %.
Healthy spinach material.						Diseased spinach material					
Leaves	0.38	2.72	55.75	2.38	17.00	Leaves	0.44	2.32	61.01	2.75	14.50
Leaves	0.38	2.66	54.58	2.38	16.63	Leaves	0.44	2.30	60.52	2.75	14.38
Leaves	0.38	2.72	55.86	2.38	17.00	Leaves	0.43	2.38	62.51	2.81	14.88
Roots	0.40	2.09	53.54	2.50	13.06	Roots	...	2.36	60.28	...	14.75
Roots	0.40	2.09	53.38	2.50	13.06	Roots	...	2.32	59.31	...	14.50
Roots	0.39	2.06	52.66	2.44	12.88	Roots	...	2.32	59.22	...	14.50

spinach and its total nitrogen, there being practically no difference in the corresponding diseased tissues. It further will be noticed that the percentage of protein and protein nitrogen is greater in the diseased tissues than in the healthy when referred to the oven-dried materials and their total nitrogen content, the only exception being the leaves which in health show a higher protein content than in disease, when calculated to the oven-dried spinach. All of which goes to show that the diseased plants are fully capable of building up proteins out of their nitrogen.

In order to establish, if possible, features characteristic of blighted spinach other than those already reported, the following experiments were carried out. Forty g. portions of spinach were repeatedly extracted with boiling hot, ammonia-free water, the combined extracts acidified with acetic acid, boiled for a few minutes, filtered, cooled and made up to 1000 cc. Of this solution representing the non-protein nitrogen, 3 portions of 25 cc. each were analyzed by the Kjeldahl method to ascertain the quantity of nitrogen present. Now 250 cc portions of this solution were treated with enough conc. hydrochloric acid to make a 20% acid, kept boiling under reflux and finally separated into the various nitrogenous groups, according to Hausmann's method, as outlined in a previous¹ paper.

Inasmuch as, by hydrolysis, peptide linkings ($\text{NH}_2\text{R}-\text{CO}-\text{NH}-\text{R}'$. COOH) are split asunder with the formation of free amino acids (NH_2R . $\text{COOH} + \text{NH}_2\text{R}'\text{COOH}$), the peptide nitrogen was ascertained by estimating the formol-titrable nitrogen in the aqueous spinach extract and subtracting this result from the formol-titrable nitrogen found in the previously hydrolyzed spinach extract. In each case coloring matter, phosphoric acid and carbon dioxide were removed from the solutions prior to their formol-titration. References concerning details² of the method as applied here as well as its limitations will be found elsewhere.³ The results obtained are presented in Table V.

¹ Jodidi and Moulton, *THIS JOURNAL*, 41, 1526 (1919).

² S. L. Jodidi, *ibid.*, 33, 1236 (1911); 34, 97 (1912).

³ S. L. Jodidi, *ibid.*, 40, 1031 (1918).

TABLE V.—DISTRIBUTION OF THE WATER-SOLUBLE NITROGEN IN SPINACH.
Data Expressed in Percentage of the Total Nitrogen of the Spinach

Materials											
Spinach material.	Acid amide nitrogen. %	Humin nitrogen. %	Basic nitrogen. %	Non-basic nitrogen. %	Peptide nitrogen. %	Spinach material	Acid amide nitrogen. %	Humin nitrogen. %	Basic nitrogen. %	Non-basic nitrogen. %	Peptide nitrogen. %
Healthy leaves	10.12	3.05	11.10	13.98	6.25	Diseased leaves	7.33	3.65	8.24	11.12	12.19
	10.11	3.02	11.11	14.91	5.34		7.31	4.31	9.31	12.62	8.98
	10.43	2.44	.	.	5.40		7.58	.	9.61	.	.
	6.10	
Healthy roots	10.64	2.91	9.83	..	.	Diseased roots	7.44	..	8.05
	10.78	3.10	9.31		7.51	2.40	8.13
	10.83	3.01	9.23	.	.		7.72	3.01	8.36

Data Expressed in Percentage of the Soluble Nitrogen of the Spinach
Materials.

Healthy leaves	21.20	6.34	23.10	26.15	12.54	Diseased leaves	15.48	7.71	17.41	23.56	25.79
	21.17	6.28	23.12	28.02	10.72		15.42	9.11	19.67	26.76	18.99
	21.85	5.08	10.84		16.00	...	20.19
	12.24	
Healthy roots	20.32	5.56	18.77	.	.	Diseased roots	18.91	...	20.20
	20.58	5.91	17.78	.	.		19.10	6.02	20.40
	20.68	5.74	17.63	.	.		19.61	7.55	20.97

Data Expressed in Percentage of the Oven-Dried Spinach Materials.

Healthy leaves	0.498	0.15	0.54	0.68	0.30	Diseased leaves	0.283	0.14	0.31	0.43	0.46
	0.488	0.15	0.54	0.73	0.26		0.273	0.16	0.35	0.50	0.34
	0.513	0.12	0.26		0.293	...	0.37
	0.30	
Healthy roots	0.415	0.11	0.38	Diseased roots	0.296	.	0.31
	0.417	0.12	0.36		0.296	0.09	0.32
	0.427	0.12	0.36		0.306	0.12	0.33

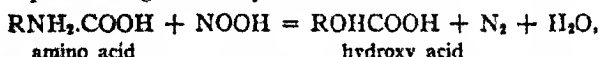
The proportion of diamino and monoamino nitrogen contained in the basic and non-basic nitrogen, respectively, was determined as follows. The phosphotungstic acid precipitate (basic nitrogen) and the filtrate from it (non-basic nitrogen) were separately treated with barium hydroxide whose excess was removed with carbon dioxide.

Filtrate and washings from the phosphotungstate, sulfate and carbonate of barium were evaporated on the water bath and finally made up to 100 cc., of which 2 portions of 20 cc. each were oxidized according to the Kjeldahl method to ascertain the quantity of nitrogen present. The remaining solution was freed from phosphoric acid and carbon dioxide as usual and formol-titrated. By this method it was ascertained in the case of

normal spinach leaves that, on an average, 41.97% of the basic nitrogen consists of diamino nitrogen, while 38.62% of the non-basic nitrogen is made up of monoamino nitrogen. In like manner it was found that, with diseased spinach leaves, the diamino nitrogen constitutes, on an average, 45.32% of the total basic nitrogen, while the monoamino nitrogen constitutes 39.75% of the total non-basic nitrogen.

Interpretation of Results.

By referring to Tables V and IV it is readily seen that the diseased tissues, especially leaves, have a smaller proportion of acid amide, basic and non-basic nitrogen, but a larger proportion of peptide and protein nitrogen than the corresponding normal tissues. It is because of these findings, together with the differences in total, nitrate, nitrite, and ammoniacal nitrogen content already reported, that we logically and forcibly come to the conclusion that the pathological condition is brought about by the process of denitrification which takes place in the spinach tissues. This process, as is well known, consists in the reduction of nitrates to nitrites and partly also to ammonia. For this reason the diseased tissues contain less nitrate but more ammoniacal nitrogen than the normal, nitrites being present in the blighted tissues only (Tables II and III). Inasmuch as nitrous acid reacts on amino acids with elimination of the amino group according to the equation



we should expect less diamino (basic) and monoamino (non-basic) nitrogen in the diseased plants than in the normal ones, which is actually the case (Table V). It is true that the amido group in some of the acid amides (asparagine) does not react chemically on nitrous acid, at least not quantitatively.¹ However, under biological conditions (existing, e. g., in the soil) the amido group in asparagine can be split off as easily as the amino group in amino acids (aspartic acid, etc.), as was demonstrated by one² of us. It was even shown that the amino group in acid amides which do not occur naturally, as in acetamide and propionamide,³ can be split off with ease under the conditions mentioned. These considerations, then, give a satisfactory explanation as to why the proportion of acid amide nitrogen is smaller in the blighted tissues than in the normal ones. Loss of elementary nitrogen by the amino acids, acid amides and nitrates, as well as loss of ammonia as such fully accounts for the fact that the diseased tissues have a smaller percentage of total nitrogen. It is, then, not to be wondered at that loss of the very important plant food, nitrogen,

¹ D. D. Van Slyke, *J. Biol. Chem.*, 9, 196 (1911).

² Jodidi, Kellogg and Snyder, *Iowa Agr. Expt. Sta. Research Bull.*, 9, 350 (1912); S. L. Jodidi, *Eighth Intern. Congr. Appl. Chem.*, 26, 129 (1912).

³ S. L. Jodidi, *J. Frank. Inst.*, 175, 250, 255 (1913).

by the spinach plants should lead to troubles chief among which is their dwarfing.

The proteins and polypeptides of the spinach tissues do not seem to have been attacked by the nitrous acid, probably for the reason that they are less soluble than the amino acids and acid amides and for the further reason that their very much larger molecules with but one amino group (at one end of the molecule) offer fewer points of attack than the smaller molecules of amino acids, each of which has one or two amino groups. The higher percentage of peptide and protein nitrogen in the diseased plants (calculated to the total nitrogen) is easily explained by the fact that here they are related to a *smaller* quantity of nitrogen, total and soluble, than in the normal plants where none of the nitrogen was lost through denitrification.

The question further arises as to why some of the attacked plants die altogether. The following contemplation seems to give a satisfactory answer. It is not out of the question that occasionally, under favorable conditions, the nitrous acid may attack proteins present in the spinach plant by reacting either on the amino group at the end of the protein molecule, or perhaps on some of the numerous CO-NH groups present. From the consideration, however, that proteins constitute an integral part of protoplasm, the carrier of life in the plant, it logically follows that a change in the chemical nature of the proteins, and hence of the protoplasm, must necessarily be fatal to the plant. This view-point is also corroborated by Loew's¹ theory according to which a substance which can act upon amino groups is a poison, and this is especially true of nitrous acid.

Summary.

The data at hand seem to warrant the following conclusions.

1. Spinach plants, especially their tops, affected with mosaic disease, have a smaller percentage of total nitrate, acid amide, mono and diamino nitrogen, but a somewhat larger percentage of ammonia than normal plants, nitrous acid being present in diseased plants only.

2. This is due to the fact that denitrification takes place whereby nitrates are reduced to nitrites which, reacting on the various nitrogenous compounds present in the spinach, bring about elimination of nitrogen in a free state, involving also loss of nitrogen in the form of ammonia.

3. Very little denitrification, if any, takes place in the roots of diseased spinach. This is evident from the fact that the differences in total, nitrate, amino nitrogen content, etc., of the roots of healthy and diseased plants are usually quite small, running sometimes in the opposite direction.

4. Conditions with regard to peptide and protein nitrogen are apparently somewhat more complicated. In the samples examined the proportion of peptide nitrogen is higher in diseased tops than in normal,

¹ "Ein natürliches System der Gift-Wirkungen," München, 1893, p. 62.

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while the proportion of protein nitrogen is higher in diseased roots than in normal, this being also true of diseased leaves when related to the total nitrogen. This is conceivable since the latter is here *smaller* due to loss through denitrification.

5. In round figures, the spinach nitrogen is made up of 55% protein nitrogen, 4.5% diamino nitrogen, 5.5% monoamino nitrogen, and 6% peptide nitrogen. This means that over 70% of the nitrogenous compounds occurring in spinach have direct nutritive value.

WASHINGTON, D. C.

NEW BOOKS.

The Metals of the Rare Earths. (Monographs on Inorganic and Physical Chemistry.) 1st edition. By JAMES F. SPENCER, B.Sc. (Vict.), D.Sc. (Liverpool), Ph.D. (Breslau), F.I.C., Lecturer in Physical and Inorganic Chemistry at Bedford College (University of London), Reader in Physical Chemistry in the University of London. Longmans, Green & Co. London, etc., 1919. x + 279 pp., with diagrams. 15 X 22.5 cm. Price, \$4.50 net.

A careful study of this work discloses the fact that the writer is extremely well acquainted with the theory and literature of this group of elements. The book is nicely arranged and is a great advance on many that have appeared in the past. The general plan followed is along similar lines to those of the best kind. The methods of analyses, and the various compounds listed under each element are described at greater length than usual. This in itself is a great recommendation, for it means so much to those who are interested in both research and study upon these metals. It appears unfortunate, however, that there is no chapter devoted to a general discussion of the various types of compounds, for, when we have elements possessing such very similar properties it is very advantageous to consider the salts from a general standpoint by directly viewing tabulated properties, etc.

Another impression gained by reading this book is that it has been written by one who has devoted much more time to the literature than to the practical side, since methods of separation which are absolutely worthless are often placed side by side with the very best without sufficient advice being given to the reader.

In several places we come across statements which indicate without proof that some of the rare earth metals are still complex. This tends to enshroud them in mystery and remove from them their simple nature which has been coming to the front more and more during recent years. It seems better for science that they be considered simple until proved complex beyond a doubt.

This book is so valuable that it is to be hoped that the author will still enlarge the space devoted to the listed compounds and correct all the errors before the next edition appears.

C. JAMES.

Principles of Chemistry. By JOEL H. HILDEBRAND, Ph.D., Associate Professor of Chemistry in the University of California pp. ix + 313. New York: The Macmillan Company, 1918

The author in the preface of this book puts forward clearly the reasons for the belief that for both teachers and students of general chemistry and qualitative analysis it is advisable to have a text in which the general principles and the fundamental theories of the science are discussed logically apart from the mass of descriptive detail which necessarily forms a part of these courses. With such a text the teacher can introduce, whenever it appears advisable, such generalizations as he desires, and the student has the opportunity to study a well-rounded discussion of the subject. As a result, the teacher is freed from following a fixed order year after year, and the student is not compelled to piece together the considerations of any principle from here and there in his text.

Acting upon this belief, the author has brought together in a comparatively small space discussions of the principles which beginners in chemistry should master in order to gain a satisfactory knowledge of the facts of general chemistry and qualitative analysis. The subjects treated include the following: kinds of matter, the kinetic theory, gas laws, weight relations, valence, equations, nomenclature, solutions, thermochemistry, speed of chemical reactions, chemical equilibrium, oxidation and reduction, periodic system, the constitution of the atom, and dispersed systems.

The book is unusually well written; the explanations are strikingly clear and simple, and the degree of emphasis put on the several topics well chosen. Many teachers will find in it simplifications of pedagogical methods which will be helpful. The book can well be recommended to students for study, whatever text is used in the course.

JAMES F. NORRIS.

Molecular Physics. By J. A. CROWTHER, 2nd edition. 187 pp. P. Blakiston's Sons and Co., Philadelphia, 1919. Price, \$1.75.

The study of subatomic phenomena has advanced so rapidly in the past 20 years that knowledge in this field is now more definite than was the atomic theory at the opening of the present century. Indeed, the time is at hand when the inductive proof that matter acts "as if" it were composed of atoms will be abandoned in chemical teaching, at an enormous saving of time and confusion, and will be replaced by the study of what Dr. Crowther calls molecular physics. Our present knowledge of the electron and the structure of the atom serves as the simplest basis for the chemical study of the elements, the periodic system, valence, atomic theory, ionization in solution, oxidation and reduction. For such a development books of this type furnish a desirable introduction.

The subjects considered are, the physics of the electron, the positive

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particle, positive ray analysis, nature and size of the electron, structure of the atom, electronic valence, radiation from the atom, the molecular theory of matter and radioactivity.

The book is amply and clearly illustrated by photographs taken almost exclusively from the original papers. Mathematics are omitted and the style is simple and comprehensible throughout. Experiments are described fully, and their immediate conclusions are given. The book is weak, however, in the deductions which are particularly interesting to chemists. The theory of electronic valence is very inadequately treated, with reference only to the opinions of English physicists, and without mention of the large amount of chemical thinking on the subject, particularly in this country. Again, only the simplest facts of radioactivity are given, with no mention of isotopy, atomic number, atomic weight, or the relation of the radioactive elements to the periodic system.

While subatomic chemistry is thus ignored, the book gives an excellent survey of subatomic or "molecular" physics and amply justifies a second edition

GERALD L. WENDT.

Lectures on the Principle of Symmetry and its Applications in all Natural Sciences.

By F. M. JAEGER, Ph D., Professor of inorganic and physical chemistry in the University of Groningen, Holland Amsterdam Publishing Company "Elsevier," London: The Cambridge University Press xii + 333 pages, 170 diagrams 17 X 25 cm. (In English)

It may not be apparent from the title of this book why it should be reviewed in *THIS JOURNAL*, for the term "symmetry" probably brings to the mind of the chemist hazy recollections of more or less profitless hours spent during his college days in the study of wooden models of crystals, the country of manufacture of which was betrayed by their accuracy in angle as well as their quite unnatural aspect. Nor is chemistry usually regarded as one of the "natural" sciences. As a matter of fact, however, this book includes much data of great value to chemists, not only by way of summary of past achievements, but also in the suggestion of lines along which work is needed.

In the first few chapters the subject of symmetry is treated from the geometrical standpoint, with numerous illustrations of different types among crystals, animals, and plants. What appears to be a new method of nomenclature of the different types of symmetry is introduced; thus the symmetry of the mineral tourmaline is denoted by C_3^V , the C standing for cyclic, the subscript 3 for the degree of symmetry (3-fold) shown by the unique axis of the crystal, and the superscript V for the presence of vertical planes of symmetry. Other terms used are D for dihedron, T and K for the endospherical cubic symmetry classes, etc.

The subject of space-lattices as related to crystal structure is naturally given full consideration; and the Barlow-Pope theory of packing of spheres

is reviewed, their so-called valency-volume hypothesis being, however, unduly praised. This is followed by a detailed explanation of the principles of the application of X-rays to the study of crystal structure, with an account of some of the results obtained. There is a chapter on mimetic forms and apparent symmetry, in which the grouping of crystals and twinning are discussed, although only a few of the possible types of "pseudo" symmetry are referred to.

The portion of the book which will appeal to chemists most is the last third, which is devoted to a very full consideration of molecular symmetry and asymmetry in chemical compounds. Starting with Pasteur's discovery of the resolution of racemic acid into 2 oppositely rotating compounds, the development of this subject is traced in considerable detail. The methods of separating the antipodes in various cases are fully described. Van't Hoff's explanation of the asymmetry of the carbon atom is shown to be the most satisfactory; and the discovery of optical activity in many other elements with valence greater than 3 is recorded. It is pointed out that configurations differing from their mirror images can be obtained even though the substituting groups are not all different; and that on the other hand it is conceivable that even when all the groups are different there may be no distortion of the central atom, and hence no optical activity. Werner's work on optically active complex inorganic compounds is of course fully reviewed, although certain of Werner's conclusions as to the relation of composition to rotatory power are shown to be improbable. The types of molecular symmetry resulting in internal compensation and impossibility of resolution into antipodes are described in detail. The connection between optical activity and the appearance of corresponding asymmetry in crystal form is discussed, and the apparent lack of agreement in many cases is pointed out.

Asymmetric syntheses form the subject of the bulk of the last chapter. Many experiments are quoted to show that "pre-existing molecular dissymmetry has a powerful guiding influence on the chemical synthesis in which new asymmetric carbon atoms are created * * * the contrast between the natural synthesis by the living organism and that by the chemist, as contended by vitalists, has mostly vanished, since the one-sidedness of natural synthesis is * * * now reduced to a merely relative difference in reaction velocities."

The book is, on the whole, well gotten up, well illustrated, and supplied with an abundance of references to papers upon the subjects discussed. The English is occasionally of a character which might be termed quaint, as for instance in the following: "As long as no exacter data about the configuration of inorganic salts are at our disposal, such applications of Werner's theory are not much promising." EDGAR T. WHERRY.

NEW BOOKS.

Technical Handbook of Oils, Fats and Waxes. Vol II, Practical and Analytical. By PERCIVAL J. FRYER, F.I.C., F.C.S., Chief Chemist and Director, Yalding Mfg. Co., Ltd, Lecturer in Oils, Fats and Waxes at the Polytechnic, Regent St., W. London Institute, and FRANK E. WESTON, BSc (1st Hons), F.I.C., Head of the Chemistry Dept., the Polytechnic, Regent St., W. Cambridge University Press, London, England, 1918. xvi + 314 pp., 69 figures. 14.5 X 22.5 cm.

This is the second volume of a very excellent work which will probably find its chief use among special students of the chemistry of oils, fats and waxes and to a lesser extent as a quick reference work in technical, consulting and industrial laboratories. The subject matter is very well planned, systematized and coördinated. The material is well selected and the sins of inclusion and omission are few. Complete references to the literature are absent, although there are some selected references no doubt judged by the authors to be the most important. The work is a valuable addition to text-books on oil and fat chemistry and will be found useful by both works analysts and students.

W. D. RICHARDSON.

Organic Chemical Reagents. By ROGER ADAMS, O KAMM and C S MARVEL, University of Illinois Bulletin, Vol. XVI, No 43. 1919 79 pp., 6 ill Price, \$0 50

Everyone will recall with gratitude how, in the dark days of 1916 and 1917, the Chemical Laboratory of the University of Illinois offered to supply the various research institutions in this country with pure organic chemicals the importation of which from abroad had been cut off. Dr. Adams and his co-workers have done pioneer work in insuring the domestic production of organic chemicals, and it is gratifying to learn from the latest catalogue of the Eastman Kodak Company that the list of these, available at the present time, contains the names of nearly 700 chemicals.

The authors of the pamphlet under review say: "During the past two years, at the University of Illinois, the methods of preparation for some of the less common organic chemicals, especially reagents in lots of one-half to five pounds, have been studied. This pamphlet contains some of the results obtained and has been printed in order that it may aid any laboratory which for one reason or another desires to manufacture these substances. The methods described are in only a few cases new ones; they are in general those which already appeared in the literature, but with such details added as will enable a man who has had a reasonable amount of experience in organic chemistry to duplicate the results without difficulty. Especial attention has been given to the explanation of why it is necessary to hold to the conditions given and what the results are providing these directions are not followed. An endeavor has also been made to use procedures adaptable to large scale production, for example, the avoiding of extractions wherever possible; the substitution of a cheap solvent for a more expensive one; or the introduction of mechanical agitation, an extremely important

factor in the success of many commercial processes." Twenty-eight preparations are covered: furfural, trimethyl-amine, amylene, trimethyl-ethylene, alkyl iodides, methylene iodide, benzoin, benzyl, benzoic acid, caproic acid, capryl alcohol, chloro-carbonic ester, α -phenyl-hydroxylamine, cupferron, isomyl nitrite, *n*-butyl nitrite, hydroxylamine, dimethylglyoxime, *p*-bromophenol, 2,4-dibromophenol, diphenyl-carbamine chloride, benzene sulfonyl chloride, thiophenol, allyl alcohol, acetyl chloride. The treatment of every compound embraces: (a) introduction, including a full bibliography; (b) preparation, or experimental part; (c) discussion of the reaction—this being based upon the personal experience of the authors with the respective compound, and is, therefore, the more welcome.

May the plans of the authors be speedily realized, and we shall look forward to the publication by them of the second pamphlet now in preparation containing the directions for 30 or more additional compounds.

M. GOMBERG.

The Preparation of Organic Compounds. By E. DE BARRY BARNETT, B.Sc., A.I.C. P. Blakiston's Sons & Co., Philadelphia. 2nd edition, 1920. pp. xiv + 273. Price, \$3.25.

This work, the first edition of which appeared in 1912, occupies a position intermediate between the well-known "Methods of Organic Chemistry" of Weyl and the more recent handbook of "Preparative Chemistry" by Vanino, the former of which consists for the most part of discussions of organic chemical methods, the latter almost exclusively of recipes compiled from the literature. For a volume of such small size, its scope is wonderfully wide; and the discussions between the descriptive matter are condensed to the smallest possible volume.

There is no question that this work should form an indispensable member of the libraries of all technical laboratories, especially of those in which the list of standard journals is incomplete. It should also be of great value to organic research workers in university laboratories; though it might be unwise for professors to encourage too free a use of it by students who are just beginning research work, as an important part of the training value of such work consists in acquiring the habit of turning directly to the original literature. "Although the present chemical curriculum is capable of very great improvement, it is to be hoped that it will not be reduced to the mere acquisition of 'useful' facts." Thus Mr. Barnett in his preface to the second edition; and it is obvious that more insight can be gained by a study of an original paper than from extracts, even when they are as carefully prepared as in the work under review.

The author has introduced a little new matter into the second edition, and it is to be hoped that a place will be found in the next for some of the synthetic work which has appeared since 1912, such, for instance, as the elegant methods of E. A. Werner for the preparation of amines. A new

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and valuable section has been added on apparatus for small-scale technical or large-scale laboratory preparations.

Certain errors may be noted, some of which are to be found in the earlier edition. Thus, on page 55, the boiling point of α -bromonaphthalene is correctly stated to be 280° , whereas on p. 53 it is given as 208° , the directions calling for the collection of the fraction $200-210^{\circ}$ (in the original paper the range is given as $270-280^{\circ}$). On p. 120 "acetophenone" is made to read "benzophenone." While desiring not to be pedantic, we would quarrel with the author's nomenclature in certain cases; thus, on p. 152 ethyl ethylmalonate is described as "ethyl diethyl malonate," and on p. 50 there is a particularly glaring instance of the indiscriminate use of "benzene" and "benzole."

The book is well set up and fairly free from misprints, and with its thinner paper and larger format it is a marked improvement over the first edition.

H. T. CLARKE.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO
CONCENTRATION. II.

BY EDWARD W. WASHBURN

Received January 19, 1920

The recent series of papers by the writer and H. J. Weiland,¹ dealing with the equivalent conductance of electrolytes in dilute aqueous solution, has recently been made the subject of adverse criticism by Kendall² and by Kraus.³

Kendall's criticism is to the effect that the method described by the writer for evaluating Λ_0 is "identical with, and founded on precisely the same assumption" as a method which Kendall employed in 1912, and is, therefore, not a new contribution, while Kraus's criticism is in substance to the general effect that the method in question is illogical, incorrect and quite unjustifiable either mathematically, physically, or chemically. As the points at issue deal with questions of fundamental importance to our interpretation of the behavior of strong electrolytes in dilute solution, it seems to the writer justifiable to discuss here in some further detail the method which he employed in evaluating Λ_0 , especially with respect to those features of it which have been adversely criticised.

¹ THIS JOURNAL, 40, 106-158 (1918).

² *Ibid.*, 40, 622 (1918).

³ *Ibid.*, 42, 1 (1920).

Kendall's Criticism.

Kendall's criticism, aside from its implication of carelessness on the part of the writer in failing to give him due credit for originating the method, would also imply that the agreement of potassium chloride with the mass-action law at high dilutions, as shown by Weiland's investigation, was due to the fact that the method of selecting Λ_0 was based upon the *a priori* assumption that within the range covered by the lowest concentrations measured, the mass-action law must be obeyed. Kendall applied his method only to acids, using it as a method for determining the conductivity of the hydrogen ion. He describes his method in the following words:¹ "The value of K_0 is found from the conductivity results of a series of dilutions by use of that particular value for the velocity of the hydrogen ion that gives values for $\frac{\alpha^2 C}{1 - \alpha}$ ($= K_E$), slowly falling as dilution increases and ultimately approaching (so far as can be perceived within the experimental error) a limiting value."

His method thus involves the assumption that within the range covered by the data there shall be a series of (*i. e.*, more than 2) values of K_E which are constant within the experimental error. Such constant values do in fact appear in all of the tables (14 to 16, inclusive) which he uses to illustrate the application of his method. There is no suggestion in his paper that he considered his method to be a special case of a more general one which would be applicable also to cases where the observed values of K_E could not be made to become even approximately constant with any value of Λ_0 which might be selected. This is further borne out by the fact that when he has to deal with strong electrolytes, Kendall entirely abandons his method and employs a method which implicitly assumes that such electrolytes will not obey the mass-action law over any finite concentration range whatever. Further, in speaking of the behavior of hydrochloric acid, he states that "the values of $\frac{\alpha^2 C}{1 - \alpha}$ certainly do fall away as dilution increases to a limiting value K_0 , but that limiting value is zero," thus apparently implying that he did not regard the value zero as necessarily inconsistent with the assumptions upon which his method was based.

Now a limiting value of zero² for K_E or an asymptotic (*i. e.*, asymptotic to the K_E axis) approach to some finite limiting value are both directly contradictory to the assumptions upon which the writer's method is based. Furthermore, his method is entirely applicable to the conduc-

¹ *J. Chem. Soc.*, 101, 1291 (1912).

² To state that the ionization constant of an electrolyte is zero is equivalent to stating that its free energy of ionization is infinite, in other words, that it is a "non-electrolyte."

tivity data for a strong electrolyte in regions where there is not the slightest evidence of obedience to the mass-action law with any value of Λ_0 which can be chosen. In these 2 fundamental respects the writer's method differs from that of Kendall, although the 2 methods will obviously outwardly resemble each other whenever the electrolyte to which they are applied actually does obey the mass-action law over a portion of the range covered by the experimental data.

To Kendall is due full credit for developing what seems to the writer the only logical method for determining Λ_0 in the case of electrolytes which obey the mass-action law within a portion of the concentration range covered by the measurements, and if the writer erred in failing to indicate the points of resemblance of his method to that of Kendall for such cases, he is glad of this opportunity to extend his apologies. The fact that Weiland's success in extending the data on potassium chloride below 0.0001 N yielded conductivity values which vary with the concentration in accordance with the mass-action law makes the writer's method, when applied to these data, resemble, apparently quite closely, the method of Kendall, since his method applied to such data will yield the same Λ_0 value.

A very important difference, between the 2 methods, however, lies in the fact that, if the conductivity values had not been found to vary with the concentration in accordance with the mass-action law, the writer's method of determining Λ_0 would still have been entirely applicable to the data, while Kendall's method would not. This can best be illustrated by applying the method to Kohlrausch's data for potassium chloride which extend only down to 0.0001 N ¹

Before doing this, however, it may be well to restate the assumptions upon which the method is based. They are as follows: (1) Potassium chloride will obey the law of mass action over some *finite* range of concentration, but this range might, of course, be far below any limit which could be reached experimentally.

(2) In the neighborhood of a few ten-thousandths N and below, the behavior of potassium chloride with respect to the mass-action law must be such that whatever the magnitude of its deviation from that law may be, this magnitude will not increase (or change its sign) with further dilution, that is, the percentage change of K_R with C will not increase as C decreases, after C has become as small as 0.0001 or 0.0002 N . There is evidently no implication in either of these assumptions that the value of Λ_0 selected must be one which causes the deviations from the mass-action

¹ In the writer's previous paper (p. 130) it was stated that the method could be employed to determine Λ_0 with an accuracy of about 0.2% in the case of conductance data which did not extend below 0.0001 N , but this statement was not further elaborated because it seemed to the writer that the applicability of the method to such data was sufficiently evident from the curves in Fig. 5 of that paper.

law to disappear gradually in the lower portion of the concentration range covered by the data, in fact as we shall show in a moment, values

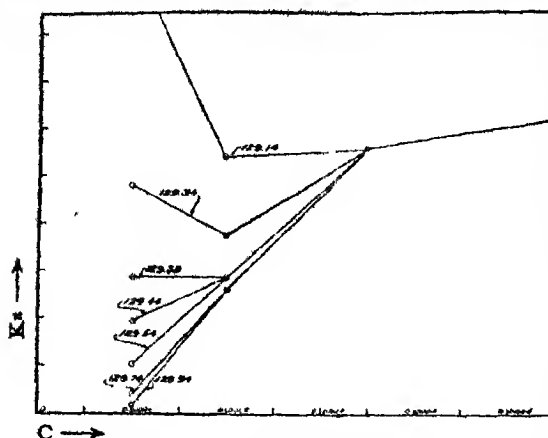


Fig. 1.

which might conceivably be assumed to produce this behavior are rejected by the method.

In order to illustrate this, a portion of Fig. 5 of the preceding paper (Fig. 2 of the present paper) lying between the concentrations 0.0001 and 0.00035 N will be magnified and instead of attempting to draw smooth

curves between points, straight lines will be used. The figure thus obtained is shown herewith (Fig. 1). In constructing this figure the values of the ordinates of the different curves have been displaced so as to cause the curves to intersect at $C = 0.00035 N$.

Applying the above 2 assumptions to this figure it is evident that the value $\Lambda_0 = 129.34$ is to be rejected and that similarly the value 129.7 (or thereabouts) is similarly to be rejected, as are all of the values which lie outside of the limits set by these two. It is evident from this figure that no value can be selected for Λ_0 which gives a behavior even approximately in accordance with the mass-action law, unless indeed the value 129.14 should be so selected on the assumption that the datum for 0.0001 N is inaccurate. Down to 0.0002 N the value 129.14 evidently gives a curve which does not deviate very markedly from the requirements of the mass-action law and if the point at 0.0001 N were rejected (and such rejection might indeed have been justified previous to Weiland's work, on the grounds that at this low concentration small errors in the conductivity or in the method of applying the water correction would have a very large influence on the computed value of K_E), the application of Kendall's method to the data for potassium chloride might point to 129.14 as the most probable value for Λ_0 . This value would, however, of course be rejected by the writer's method, which method does indeed not directly determine the value of Λ_0 at all, but merely places an upper and lower limit on it. The method is thus not a method of selection but rather a criterion for rejection.¹

¹ (Note by James Kendall).—"I am entirely in agreement with the differentiation

Kraus's Criticisms.

The first part of Kraus's paper is devoted to a mathematical analysis of the $K_E - C$ curve and this analysis is, in the main, accurate for the assumptions which he makes. In the interests of exactness the following points may be noted, however. The 2 sentences immediately following his Equation XI are exact statements only if the values assumed for Λ_0 are greater than approximately 129.65 in the first statement, and 129.5 in the second. The statement immediately following his inequality No. XII is obviously true, but in the writer's opinion the most important part of the statement is the conditional clause which introduces it. One of the fundamental differences in the view points of Kraus and the writer is brought out in the paragraph immediately following his inequality No. XIII. The writer is unable to see any force whatever in the arguments which he there advances.

In the previous paper by Kraus and Bray, these authors fitted to the conductance curve for potassium chloride the following empirical equation:

$$\frac{\Lambda^2 C}{a(a - \Lambda)} = b + c \left(C \frac{\Lambda}{a} \right)^d,$$

in which a , b , c and d are parameters to be evaluated from the data. They were able to fit the equation to the data, with satisfactory agreement, from the concentration $C = 3 N$ down to $C = 0.001 N$, but below the latter concentration the equation did not agree with the experimental data of Kohlrausch. Because of this, they argued that Kohlrausch's data below $0.001 N$ were incorrect, stating that it would be "an unjustifiable procedure to assume, after showing that a certain dilution law holds from $3 N$ to $0.001 N$ within the limits of experimental error, that the law suddenly undergoes an enormous change after reaching a dilution where there is good reason from a theoretical standpoint for believing that the law must hold."

This line of reasoning has already been discussed by the writer in his previous paper and the discussion need not be repeated here. Since the measurements by Weiland have confirmed those of Kohlrausch, Kraus in his last paper (p. 15) rejects the above conclusion of Kraus and Bray, but seeks, nevertheless, to retain intact the argument which lead to that conclusion, that is, since his equation cannot be fitted to the whole conductance curve from $3 N$ down, he proceeds, so to speak, to pull the equation down the curve so as to start it at about $0.02 N$ instead of $3 N$. Then by re-evaluating the 4 parameters (and incidentally obtaining quite different values for them) he finds, not unnaturally, that the equation can be fitted satisfactorily to all of the lower end of the curve.

here drawn by Prof. Washburn between our respective methods for the determination of Λ_0 , and extend my apologies in return to Prof. Washburn if I have erred in directing attention too strongly to the striking points of similarity which they exhibit."

Now the extrapolation of such purely empirical functions will naturally give as many different results for Δ_0 and K_0 as there are different kinds of empirical functions which can be fitted to the experimental data within the range open to measurement, and in this respect there is no particular virtue in the Kraus empirical function over others (for example, the Bates function), which might be equally satisfactorily fitted to the experimental portion of the curve. In fact we can never hope to determine Δ_0 and K_0 with any feeling of confidence unless the determination can be based upon some guiding principle other than the mere extrapolation of some one of the various empirical functions which might be fitted to the experimental data. The method employed by the writer is based upon such a guiding principle and if the principle in question is admitted to be reasonable (which Kraus does not admit), the method of employing it is mathematically sound. Before going into further detail concerning the reasons for making the assumptions upon which the method is based, we will first consider in sequence some of the specific criticisms which Kraus makes of the method and of the manner in which it is applied.

(1) On page 8 of his paper Kraus advances the opinion that an "erratic behavior" of a curve is to be judged not alone by the form of the primitive function but also by any unusual changes in its derivatives. He then proceeds to show that the first and second derivatives of the $K_E - C$ graph obtained by the writer's method are rather complex in their behavior. The argument that a given type of regular and smooth curve is to be condemned on the ground that its higher derivatives go through some rather rapid changes in certain regions, is at least a novel one. If potassium chloride is to obey the mass-action law over any finite range of concentration whatever, the $K_E - C$ curve *must* evidently be of exactly the type which the writer's method of extrapolation gives and its higher derivatives *must* exhibit the behavior which Kraus indicates. His condemnation of the method on the grounds of this behavior is, therefore, only a reiteration in other terms of his own view that it is unreasonable to assume that such electrolytes will obey the mass-action law within any finite concentration range whatever. Incidentally it may be noted that the atomic-heat curves of all the solid elements and the Debye and the Nernst-Lindemann equations which express them, have the same general form as the $K_E - C$ curve which Kraus condemns and their higher derivatives will exhibit the same "remarkable behavior," upon which he bases this condemnation. The reason why Kraus's own function can never exhibit such a behavior is, of course, merely because of its exponential form. There are plenty of other types of empirical functions which could be fitted just as satisfactorily to the data but whose derivatives would, of course, not behave like those of his exponential function.

(2) On p. 10 Kraus states that the writer's first assumption, namely,

that the values of K_E will eventually gradually approach a constant at extreme dilutions, is not fulfilled by the method of extrapolation. This statement is perhaps due to a misunderstanding. The expression "gradual approach to a constant limiting value," was intended to mean simply an *eventual* perpendicular approach to the E_E axis attained by a gradual and smooth decrease in K_E with decreasing C , and this assumption is certainly entirely consistent with the method of extrapolation employed.¹

(3) Kraus further concludes (p. 12) that the writer's statement, "that no assumption is made as to the actual path over which values of K_E will approach the constant limiting value * * * * " is not correct, on the ground that this method of extrapolation is based on the assumption that K_E approaches its limiting value horizontally. Of course it is based upon this assumption, this being, as stated above, the first of the 2 assumptions which constitute the principle of the method, but nevertheless no assumption is made as to a particular mathematical equation with numerical parameters determined by the measured portion of the curve, which rigidly fixes the path of the curve below the lowest measured point. In this essential respect it differs from all of the "empirical function" methods of extrapolating.

(4) Kraus then criticises (p. 13) adversely Weiland's procedure by which he first treats individually each of his 4 series of measurements, subsequently averaging the results thus obtained. If there had existed only one set of measurements certainly no objections could have been made to treating this set by itself. It is difficult to see how the fact that more than one series of measurements was made should be considered an objection to the initial treatment of each series by itself, even without the suggestion of any possible cause for the slight differences among the different series. Kraus also objects to Weiland's suggestion that the cause of the slight differences among the different series might be small variations in the cell constant. He bases this objection upon the fact that in the cases of 2 of the 4 series finally employed (and a third one which was rejected), the concentrations were extended sufficiently high to enable the cell constant to be determined by comparison with Kohlrausch's data and that in these cases the cell constants were found to be identical within the experimental error. Whether or not the apparent deviations are to be ascribed to slight variations in the cell constant this seems hardly adequate grounds for objecting to the initial treatment of each series as consistent within itself. Moreover, it should be noted that a variation

¹ It is true that the method could still be formally applied if the first assumption were dropped and only the second one used, but without the first assumption the second one would appear to be entirely arbitrary, because there would then be no particular reason why it should be valid. The 2 assumptions are complementary and together constitute a logical and reasonable principle upon which to base the determination of Λ_∞ .

in the cell constant, too small to be detected by comparison of the conductances of a $0.0001\ N$ solution at the end of 2 different runs, might still be large enough to produce very appreciable differences in the K_E values calculated from measurements below $0.00005\ N$. Since with the data obtained in a single run, the cell constant cancels out of the mass-action expression, the procedure of initially treating each series by itself in order to eliminate any possibility of error due to a slight change in the cell constant is certainly not an illogical one.

(5) Kraus then advances the criticism (p. 13) that since the interpolation curves drawn by Weiland through his experimental points approximate straight lines, a tacit assumption, namely, that of linearity, is made, as to the manner in which the curves should proceed. It is difficult to understand how Kraus can offer this as an objection since in the preceding sentence he admits that Weiland's curves lie within the limits of the experimental errors. It is certainly a sound procedure for interpolation purposes to put a straight line, rather than some more complicated curve, through a series of experimental points, if the straight line fits the data within the experimental error. Such a procedure, of course, does not assume that some other type of curve might not also be drawn through the points and reproduce the data equally well.

If, however, as in this case, the data *require* a straight line or a curve approximating to it, it is hard to see why drawing such a curve can contain "a tacit assumption as to the manner in which the curves should proceed." The manner in which the curves should proceed is, within the experimental error of the data, determined by the loci of the observed points and not by any kind of assumption which it is possible to make, unless indeed one wished to admit the reasonableness of putting an *oscillating* curve through the points.

(6) On p. 14 Kraus makes a series of statements which he sums up in the following sentence: "In fact an extrapolation to zero concentration by Washburn's method cannot give a correct result unless the curve in the experimental region is a straight line in the C - A plot," and he goes on further to point out the obvious fact that it is possible to pass a great many curves through Weiland's observed points, all lying within the limits of experimental error. He then finally concludes that the "true form *

* * * * is one convex toward the C -axis and not a straight line as Weiland and Washburn tacitly assume."

To these criticisms the writer must most emphatically demur. The result obtained by the writer's method of extrapolation is *not dependent* upon the passing of a straight line through the observed points. The method is entirely applicable, as already explained in the first part of this paper, *even though the points do not lie on a straight line or on anything resembling a straight line*. Furthermore, any empirical function which

will express Weiland's data within the limits of experimental error, provided, of course, that some oscillating function like a sinusoidal curve is not employed, may be used (instead of the objectionable "straight line") for interpolating the values which are employed in constructing the family of K_E — C curves shown in Fig. 2. This can be illustrated, for example, by taking Kraus's own function which he has fitted to these data and which, according to his own arguments, possesses all the desirable qualities which such a function should have, and employing it for the purpose of

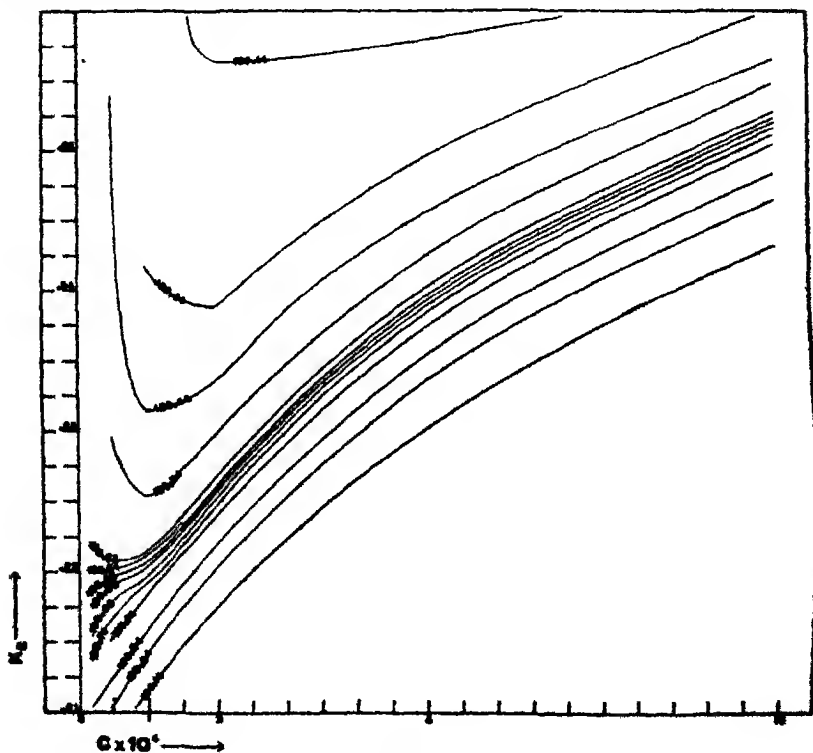


Fig. 2,

interpolating the necessary values for constructing the family of curves. If this is done a family of curves identical with that shown in Fig. 2 will be obtained, except that the central curve from which the others branch off will have the value of 129.65 instead of 129.64. In fact the only result of using different interpolation curves through the experimental points is to change slightly the A_0 value of this central curve of the family, a behavior which is in fact clearly illustrated by Weiland's own treatment of his 4 curves.¹

¹ See Fig. 12, p. 143 of his paper.

The different curves in Fig. 2 are due to the selection of different assumed values for Λ_0 . Among these various curves the criterion which the writer employs says that the true value of Λ_0 belongs to a curve lying between the 2 limits determined by the curves marked 129.63 and 129.65, while Kraus claims that the correct curve is the one marked 129.9. From studying this figure, it is difficult to see any reason whatever for selecting from the various curves there shown, the one marked 129.9 and claiming that it is the correct one. Certainly the selection of this curve must apparently be made without any adequate guiding principle. The curves marked 129.7 to 130.1 in the lower part of the figure appear to have no distinguishing characteristics which offer a basis for selecting one of them in preference to the others. The rejection of curve 129.63 and those above it and of curve 129.65 and those below it, however, is based upon the thoroughly reasonable assumption that immediately below the concentration 0.00005 N the mass action expression for potassium chloride is not going to change with the concentration at a more rapid rate than it does at concentrations immediately higher, nor is the rate of change going to alter in sign.

The reasons for the 2 fundamental assumptions employed by the writer are the following. (1) The mass-action law is a direct deduction from the Second Law of Thermodynamics for any chemical equilibrium in a solution within which the thermodynamic environment of the reacting species remains constant. This will be the case whenever the solution is so dilute that the nature of the environment of each reacting species is determined entirely by the properties of the water molecules which surround it, the other ions and molecules being too far away to exert an appreciable influence upon its environment. In the nature of the case this condition will be attained after sufficient dilution but the degree of dilution required cannot, of course, be predicted in advance.

(2) The second assumption, namely, that, after a dilution of 5,- or 10,000 liters has been reached, the deviation from the mass-action law $\left(i. e., \frac{1}{K_E} \frac{dK_E}{dC} \right)$ will thereafter not at any rate increase with further dilution or change in sign, is perhaps more difficult to justify by formal reasoning. The selection of the particular dilution limits named is admittedly based largely upon "physico-chemical instinct" arising out of the whole body of knowledge which we have concerning the behavior of dilute solutions. In a 0.0001 N solution of potassium chloride the solute particles are on the average separated from one another by a distance of 60 water molecules and it seems not unreasonable to suppose that further separation will not at all events *accelerate* the rate at which the molal fugacity of any of the species is changing with the concentration.

The method employed by Kraus for evaluating Λ_0 is based upon, or

at all events involves, the assumption that the magnitude of the deviation of potassium chloride from the mass action law $\left(i. e., \frac{1}{K_E} \frac{dK_E}{dC} \right)$ increases with dilution at a constantly accelerated rate until it finally reaches an infinite value at $C = 0$. His assumption is thus the exact opposite of the one employed by the writer, or mathematically expressed:

$$\lim_{C \rightarrow 0} \frac{1}{K_E} \frac{dK_E}{dC} = 0 \quad (\text{Washburn})$$

$$\lim_{C \rightarrow 0} \frac{1}{K_E} \frac{dK_E}{dC} = -\infty \quad (\text{Kraus}).$$

URBANA, ILLINOIS

THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO CONCENTRATION. A REPLY.

BY CHARLES A. KRAUS,

Received February 27, 1920.

Through the kindness of the Editor of THIS JOURNAL, the foregoing article by Dr. Washburn was submitted to the writer in manuscript form for reply. The various points of difference have for the most part been treated sufficiently in the preceding papers and need not be discussed further here. However, Dr. Washburn has made his position somewhat clearer in certain respects and has raised one or two new points which may be considered further.

In the first place, Dr. Washburn now states that the mass-action law is assumed to hold at finite concentrations.¹ Without entering into a discussion of the probability of the correctness of this assumption from a physical point of view, it is at once clear that this is, indeed, the fundamental element underlying Dr. Washburn's position. In his method of extrapolation he assumes the mass-action law to hold. The graphical means employed to carry out the extrapolation naturally conform to this assumption and the extrapolated values are necessarily in harmony with it. The fallacy lies in that the agreement of the extrapolated values with the mass-action law are looked upon as a proof that this law holds, whereas, in fact, such agreement is merely a consequence of the assumption made. Naturally, somewhat the same condition prevails in the case of any extrapolation. The extrapolated values necessarily agree with the functional relation assumed in carrying out the extrapolation. There is this difference, however, in the 2 cases: Dr. Washburn's extrapolation function holds only for the last point of the experimentally determined curve, while other methods employ a function which holds over a considerable range of concentration. The greater the range of experimentally deter-

¹ Washburn, THIS JOURNAL, 42, 1079 (1920).

puted values that can be accounted for by means of the function in question, the greater the probability that the extrapolated values lie within a given limit of precision.

As Dr. Washburn himself points out, his method of extrapolation may be applied to a solution at any concentration and for any form of conductance curve. This is obviously the case, since he assumes his function to hold only for the last experimentally determined point; in other words, the function does not hold over an appreciable range of concentration in the regions where measurements exist and it may, therefore, always be applied. It follows, further, that the agreement of his extrapolated values with the measured values will always be equally good, *i. e.*, they will hold exactly at the last point.

This is illustrated in the following table, in which are given values of K and Λ_0 as determined by extrapolation by Dr. Washburn's method, for the intervals 10^{-3} to $10^{-4} N$ and 10^{-2} to $10^{-3} N$, together with the values of $K'(K_E)$, at different concentrations. The values relate to potassium chloride in water at 18° and the data are taken from the work of Kohlrausch and Maltby.

TABLE I.—VALUES OF K' AND Λ_0 OVER DIFFERENT CONCENTRATION INTERVALS
ACCORDING TO WASHBURN'S METHOD

C	10^{-4}	1.5×10^{-4}	2×10^{-4}	3×10^{-4}	5×10^{-4}	7×10^{-4}	10^{-3}
K'	0.03605	0.03612	0.03626	0.03878	0.04634	0.05282	0.05860
$K = 0.03605, \Lambda_0 = 129.408$							
C	10^{-3}	1.5×10^{-3}	2×10^{-3}	3×10^{-3}	5×10^{-3}	7×10^{-3}	10^{-2}
K'	0.1147	0.1151	0.1165	0.1267	0.1594	0.1686	0.1941
$K = 0.1147, \Lambda_0 = 128.372$							

It will be seen that in both intervals K' decreases and gradually approaches a limiting value. For the interval 10^{-3} to $10^{-4} N$ we obtain the limiting values $K = 0.03605$ and $\Lambda_0 = 129.408$, while for the interval 10^{-2} to $10^{-3} N$ we obtain the values $K = 0.1147$ and $\Lambda_0 = 128.372$. It is evident that Dr. Washburn's method may be applied to any concentration interval and it will in every case be found that the extrapolated values conform to the mass-action law at the end of this interval. But the values of Λ_0 and K determined in this way will be different for different intervals. If, therefore, the method is applied to the last points at which experimental data are available, it will appear that the point has just been reached where the mass-action law applies. But this condition was assumed in the first place, and the apparent agreement is without weight in determining whether or not the mass-action law really holds.

In principle, Dr. Washburn's method is not new. The same method was employed by Wegscheider,¹ the only essential difference being that Wegscheider did not employ graphical means in carrying out the extrapolation. He showed, however, that a value of Λ_0 may be assumed such

¹ Wegscheider, *Z. physik. Chem.*, 69, 603 (1909).

that the points for a limited concentration interval conform to the mass-action law within the limits of experimental error. Obviously, such a result may be obtained at any point of the conductance concentration curve and, if the point chosen be the last point for which experimental data are available, then it will appear that the mass-action law is approached in the manner which Dr. Washburn has found in the case of Weiland's measurements. Other investigators have likewise employed this method of extrapolation, notably Dutoit in dilute non-aqueous solutions.¹

In the treatment of his results Weiland has drawn his individual curves as well as his average curve in such a manner as to conform approximately to the mass-action law between the last 2 interpolated points. Dr. Washburn defends Weiland's method of treating his results as individual series and the manner of drawing his curves. If the relative precision in a given series of measurements is sufficiently high with respect to the precision obtained in different series, then this method of treatment may be justified. There is, however, much doubt as to whether Weiland actually attained a sufficient precision to justify such a procedure. In any case, if the different series have sufficient precision so that they may be treated individually, then the curve which is drawn through the points in any series should as nearly as possible pass through all the points. Of course, in drawing a curve in the case of the C , Λ -plot, it would hardly be permissible to assume a high degree of complexity, since at higher concentration it is known that the curve is of comparatively simple form and it is improbable that the curve becomes more complex at lower concentrations. In any case, if it is possible to pass a simple form of curve through a given series of points, the curve should unquestionably be so drawn. But this has not been done in Weiland's treatment of his result. Weiland's data not only do not require that a straight line should be drawn through them, as Washburn states,² but they do require that a curve should be drawn through them and this curve is in general convex toward the C -axis but in no case concave. Neither the points of individual series nor the points of the average curve actually conform to the curves as Weiland has drawn them. As stated in the writer's previous article, the curves for the individual series are for the most part convex toward the axis of concentrations, particularly in the more dilute solutions, while none of them are concave toward this axis, which result might reasonably be expected if the true form of the curve were a straight line, i. e., if the mass-action law applied. So, too, if the value of all the determinations are averaged, they yield a curve distinctly convex toward

¹ Dutoit and Duperthuis, *J. chim. phys.*, 6, 705 (1908), Dutoit and Gyr, *ibid.*, 7, 198 (1909).

² Washburn, *loc. cit.*, p. 1084.

the axis of concentration, thus precluding the conclusion that the mass-action law applies within the range of concentrations actually measured.

In his last paper, Dr. Washburn claims that his method of extrapolation is independent of the nature of the interpolation function employed in obtaining values on a smooth curve at round concentrations.¹ He claims, in fact, that the values interpolated by means of the writer's function yield, when treated according to his (Dr. Washburn's) method, the value $\Lambda_0 = 129.65$, a value practically identical with that deduced by Weiland. This is not correct. If the writer's interpolated values are treated in this way, the value $\Lambda_0 = 129.74$ will be obtained corresponding to the tangent $\Lambda_0' - P$ as shown in Fig. 4 of the writer's previous article.² The value $\Lambda_0 = 129.65$ corresponds approximately to the tangent $\Lambda_{0.1} - P'$ of the same figure. In this case the value assumed for the conductance at the concentration corresponding to the point P does not represent a value interpolated by means of the writer's function.

As was pointed out above, Washburn's method may indeed be applied to any form of curve and at any concentration, but the value of Λ_0 will be different for the different concentrations and for the different forms of curves, save in the exceptional case that Λ is a linear function of the concentration, in which case the mass action law is actually obeyed.

It is evident that, in order to demonstrate that the mass-action law applies, it must be shown that the points in the Λ, C -plot lie on a straight line; that is, that a straight line will represent the results within a smaller limit of error than any other simple type of curve. This Weiland's measurements do not do. The average values of his measurements yield a curve distinctly convex toward the C -axis. Weiland's results, therefore, indicate that the mass-action law does not hold up to $2 \times 10^{-3} N$.

WORCHESTER, MASS

THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO CONCENTRATION. FINAL REJOINDER.

BY EDWARD W. WASHBURN.

Received April 6, 1920.

From Kraus' latest contribution to the discussion of the above topic it is evident that the writer has failed entirely to make clear the nature of his method of extrapolation and its essential differences from previous methods. Despairing of his ability to improve the lucidity of his previous attempts, the writer desires only to add one more illustration in further refutation of Kraus' reiterated claim, that the character of the results obtained arise from the asserted "linear" nature of the interpolation curve which Weiland passed through his observed points, this interpola-

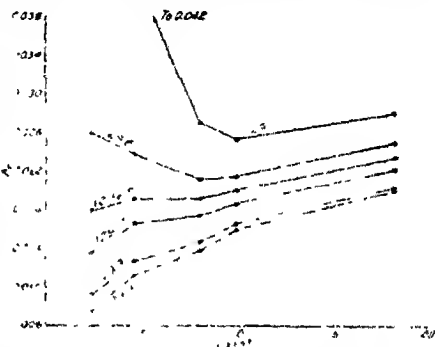
¹ Washburn, *loc. cit.*, p. 1084

² THIS JOURNAL, 42, 11 (1920).

tion curve being incorrect and unjustified according to Kraus' point of view.

Now obviously one way of avoiding all question on this point is to abandon entirely the use of any interpolation curve and to apply the extrapolation method directly to the observed points. By such a method of procedure one, of course, loses the very desirable advantage of smoothing out the irregularities of the observations, these irregularities naturally appearing in a very highly magnified form in the $K_c - C$ diagram, but at all events no allegation of personal bias as to the proper locus and course of the $C - \lambda$ curve can be brought against the method.

Of the several series of measurements made by Weiland, one, that of January 24, contains 5 measured points ranging from 2 to 180 micro-equivalents per liter. Moreover, as evident from Fig. 10 of Weiland's paper, the points of this series are not only more numerous and regular than those of any other series, but by their location they evidently represent more nearly the average of



all the measurements than do those of any other series. We shall, therefore, employ directly this series of points for extrapolation. In this way the graphs shown in the accompanying figure are obtained, all attempts at smoothing being also avoided here. From these graphs the writer's method of extrapolation evidently places the true λ_0 value between 129.60 and 129.70, the most probable value being about 129.64 or 129.65, and this value is selected not at all for the reason that it gives results in agreement with the mass-action law, but for reasons which have been sufficiently explained above.

The above conclusion is, of course, wholly dependent upon the assumption that the data employed are correct and is valid only insofar as they are correct. Anyone is, of course, at liberty to claim that Weiland's data do not have the accuracy which their consistency with one another would seem to indicate and such a claim may indeed be true. Certainly the writer would not go so far as to assert the contrary, but until experimental proof of their inaccuracy is brought forward they are entitled to acceptance, at least tentatively, at their face value. To do otherwise would resemble too much Kraus' former proposal to reject Kohlrausch's data below 0.001 N because they did not harmonize with the empirical function which he had succeeded in fitting to the data above that point.

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF WARSAW.]

THE RESTATEMENT AND CORRECTION OF THE THERMO-CHEMICAL DATA ON ORGANIC COMPOUNDS.

I. THE DATA OF P. W. ZUBOW.¹

BY W. SWIETOSLAWSKI.

Received February 4, 1920

In 1917 I published in *THIS JOURNAL*² a discussion of the necessity of accepting and introducing a standard unit into the thermochemistry of organic compounds, with a view to the correction of all measurements performed by means of the calorimetric bomb.

Before this standard unit should be accepted and established by an authoritative body, I proposed, for the determination of the constant of a calorimetric bomb, the combustion of the following substances and the acceptance of the following heats of combustion:

Naphthalene	9612 cal	} Expressed in 15° cal For 1 g of substance Weight in air (v constant)
Benzoic acid	6311 cal	
Cane sugar	3945 cal	

The above-mentioned paper states the reasons for accepting these numbers as the most probable. The heat of combustion of naphthalene especially can be considered as very exactly measured, because the determinations performed in 2 different laboratories (in the Bureau of Standards at Washington by Mr. Dickinson, and in the Lougine's Thermochemical Laboratory by myself) had given the identical values of 9612 cal. $\pm 0.01\%$. It is also very probable that 2 other values, 6311 and 3945, are correct within $\pm 0.05\%$. If we accept the cited data as a provisional basis for the thermochemistry of organic compounds, we can then set about to correct the thermochemical data of previous investigators. This problem cannot be deferred, because at present we are already lost in conjectures about the conditions which might have influenced the M. Berthelot's, W. Lougine's, Stohmann's, and all other previous investigators' measurements.

¹ Note by P. W. Zubow:

"I pointed out formerly that the values given by my determinations were too large and explained this by the hypothesis that the heat capacity of my bomb had been erroneously determined. To correct my data, I had intended to make a new determination of the heat capacity, but I put off this experiment, believing that my values were comparable with each other, and relatively true and exact. The investigations of W. Swietoslawski have shown that the correction of my data can be performed without a new determination of the heat capacity of the bomb. The correction of my data by means of a constant factor had been often discussed with W. Swietoslawski and when the latter raised the question of introducing a standard unit into thermochemistry and correcting all previous thermochemical data, I expressed my pleasure at his proposal to recalculate my measurements. For this purpose I have delivered to W. Swietoslawski all my experimental data.—P. W. ZUBOW."

² *THIS JOURNAL*, 39, 2595 (1917).

In another paper corrections will be published which ought to be introduced in the measurements of the above mentioned authors. In this communication will be given the corrected data of P. W. Zubow; the results of measurements performed with the greatest accuracy and precision in Louguine's Thermochemical Laboratory at Moscow in 1892-1910.

It is to be noted that the data of Zubow are especially important, because the heat capacity of his apparatus was determined by the same method as that used by M. Berthelot in his first measurements, besides which Zubow's calorimetric bomb was made by Golaz in Paris at the same time as M. Berthelot's bomb, and the constant of the apparatus was determined by the combustion of naphthalene, accepting for the heat of combustion the first data of Berthelot, obtained in 1887. This circumstance is very important, because it will facilitate in the future the solution of several problems, by correcting the earlier thermochemical data.

The correction of Zubow's data does not involve any difficulty, inasmuch as the author has furnished me with all his experimental data, beginning with those of 1892, and has rendered possible in this way the complete reconsideration of the whole question. Moreover the combustion of naphthalene, which was performed by Zubow with the greatest precision, facilitated the computation of the factor necessary for correcting his data.

If we accept 9612 cal. as the heat of combustion of naphthalene, for one gram weighed in air, and consider that Zubow obtained the value 9706 cal. $\approx 0.03\%$, we obtain the factor:

$$\alpha = \frac{9612}{9706} = 0.9907$$

Denoting the heat of combustion as given in Zubow's previous publications by A_{un} , we then obtain as the corrected value A_{cor} .

$$A_{cor} = \alpha A_{un} = 0.9907 A_{un}.$$

This value corresponds to the heat of combustion of 1 g. of liquid or solid substance burned at 18°, at constant volume.

In Tables I to VI are given the corrected values for 40 hydrocarbons, 41 alcohols, 23 ketones, 7 esters, 9 acids and 6 compounds containing nitrogen.

In these tables A_{un} indicates Zubow's uncorrected data; A_{cor} , the heat of combustion of one gram of substance weighed in air; A_{mol} (*v* const. or *p* const.), the heat of combustion of one mole of substance, weighed in air; $A_{mol (abs.)}$ —the molecular heat of combustion of substance, weighed in a vacuum; W'_{18} , the correction for the gaseous state of the substance, when *t*° indicate the boiling point. The last values were computed from the specific heats c_{18} , and the heats of evaporation W_i of the substances

TABLE I—HYDROCARBONS

No.	Formula	Name	M	A_{atm} ($r=\text{const.}$)	A_{cor} ($r=\text{const.}$)	A_{mol} ($t=\text{const.}$)	A_{mol} ($p=\text{const.}$)	A_{mol} (obs.) ($p=\text{const.}$)	W_{18}	A_{gas} ($p=\text{const.}$) No.
1	C_3H_{10}	Trimethyl ethylene	70 08	11466 3	11355 1	795 8	797 3	796 0	7 2	803 2 1
2	C_4H_{16}	Methyl-cyclobutane	70 08	11293 1	11183 6	783 7	785 2	784 2	7 9	792 1 2
3	C_5H_{18}	Cyclopentane	70 08	11284 1	11174 6	783 1	784 6	783 6	7 9	791 5 3
4	C_6H_{20}	Dihydro-benzene	80 06	10306 9	10405 0	833 0	834 2	833 2	9 9	843 1 4
5	C_7H_{24}	Dimethyl-methylene-cyclopropane	82 08	11043 7	10936 6	897 7	899 2	898 0	8 9	906 9 5
6	C_8H_{28}	Cyclohexene	82 08	10962 0	10855 7	891 0	892 5	891 2	9 7	900 9 6
7	C_9H_{32}	Methyl-cyclopentane	84 10	11258 2	11149 0	937 6	939 3	937 9	9 5	947 4 7
8	$\text{C}_{10}\text{H}_{36}$	Cyclohexane	84 10	11217 4	11128 4	935 9	937 6	936 3	9 9	946 2 8
9	$\text{C}_{11}\text{H}_{40}$	Heptene	84 10	11435 2	11324 3	952 4	954 1	952 6	9 3	961 9 9
10	$\text{C}_{12}\text{H}_{44}$	α -Hexane	86 11	11602 6	11490 0	989 4	991 4	989 8	8 7	998 5 10
11	$\text{C}_{13}\text{H}_{48}$	Methyl-1-cyclohexene-1	96 10	10935 8	10829 7	1040 7	1042 4	1040 9	12 7	1033 6 11
12	$\text{C}_{14}\text{H}_{52}$	Methyl-1-cyclohexene-3	96 10	10963 0	10856 7	1043 3	1045 0	1043 6	12 3	1035 9 12
13	$\text{C}_{15}\text{H}_{56}$	Methylene-cyclohexane	96 10	10967 8	10861 4	1043 8	1045 5	1044 1	12 5	1036 6 13
14	$\text{C}_{16}\text{H}_{60}$	Bicycloheptane	96 10	10928 2	10822 2	1030 0	1031 7	1030 3	12 2	1042 5 14
15	$\text{C}_{17}\text{H}_{64}$	Cycloheptene	98 11	11219 4	10921 2	1049 5	1051 3	1049 9	13 1	1063 0 15
16	$\text{C}_{18}\text{H}_{68}$	1,3-Dimethyl-cyclopentane	98 11	11219 4	11110 6	1091 1	1092 1	1090 7	11 4	1102 1 16
17	$\text{C}_{19}\text{H}_{72}$	Methyl-cyclohexane	98 11	11233 0	11124 0	1091 4	1093 4	1091 8	12 4	1104 2 17
18	$\text{C}_{20}\text{H}_{76}$	Cycloheptane	98 11	11186 4	11077 9	1086 9	1088 9	1087 3	13 3	1100 6 18
19	$\text{C}_{21}\text{H}_{80}$	1,3-Dimethyl-dihydrobenzene	108 10	10734 5	10620 5	1148 1	1149 8	1148 2	14 5	1162 7 19

20	C_8H_{16}	1,1,2-Trimethyl-cyclopentene-2 (is-laurolene)	110 11	10939 8	10833 7	1192 9	1194 9	1193 3	13 4	1206 7	20
21	C_8H_{16}	Laurolene	110 11	10934 2	10828 1	1192 3	1194 3	1192 7	14 3	1207 0	21
22	C_8H_{16}	1,3-Dimethyl-cyclohexene-3	110 11	10950 7	108 445	1194 1	1196 1	1194 5	15 0	1209 5	22
23	C_8H_{16}	1,2,4-Trimethyl-cyclopentane	112 13	11211 8	11103 0	1245 0	1247 3	1245 4	13 8	1259 2	23
24	C_8H_{16}	1,1,7-Trimethyl-cyclohexane	112 13	11185 5	11077 0	1242 1	1244 4	1242 5	13 9	1256 4	24
25	C_8H_{16}	1,3-Dimethyl-cyclohexane	112 13	11144 1	11036 0	1237 5	1239 8	1238 0	14 4	1252 4	25
26	C_8H_{16}	1,4-Dimethyl-cyclohexane	112 13	11061 5	10954 2	1228 3	1230 6	1228 8	14 4	1243 2	26
27	C_8H_{16}	Methyl-cycloheptane	112 13	11203 6	11094 9	1244 1	1246 4	1244 5	15 7	1260 2	27
28	C_8H_{16}	n-Octane	114 14	11519 9	11408 1	1302 1	1304 7	1302 7	15 0	1317 7	28
29	C_8H_{16}	Methyl-1-n-propyl-cyclopentane	126 14	11213 3	11104 5	1400 7	1403 3	1401 4	17 5	1418 9	29
30	C_8H_{16}	1,2,3-Trimethyl cyclohexane	126 14	11169 0	11060 7	1395 2	1397 8	1395 9	17 4	1413 3	30
31	C_8H_{16}	1,3,3-Trimethyl-cyclohexane	126 14	11159 1	11050 9	1394 0	1396 6	1394 7	16 8	1411 5	31
32	C_8H_{16}	Ethyl-cycloheptane	126 14	11256 2	11147 0	1406 1	1408 7	1406 5	19 3	1426 1	32
33	$C_{10}H_{18}$	l Limonene	116 13	10866 6	10701 8	1456 8	1459 1	1457 2	19 4	1476 6	33
34	$C_{10}H_{18}$	l Pinene	116 13	10924 5	10819 5	1472 7	1475 0	1473 2	18 7	1491 9	34
35	$C_{10}H_{18}$	d-Pinene	116 13	10914 6	10808 7	1471 4	1473 7	1471 9	18 7	1490 6	35
36	$C_{10}H_{18}$	Phenanthene	138 14	10980 3	10873 8	1502 1	1504 7	1502 8	19 3	1522 1	36
37	$C_{10}H_{18}$	Methyl-1-n-propyl-3-cyclohexane	140 16	11168 7	11060 4	1550 2	1553 1	1550 9	21 9	1572 8	37
38	$C_{10}H_{18}$	Caromenthane	140 16	10907 0	10801 2	1513 9	1516 8	1514 6	21 9	1536 5	38
39	$C_{10}H_{18}$	n-Decane	142 18	11438 8	11327 8	1610 6	1613 8	1610 2	20 2	1630 4	39
40	$C_{10}H_{18}$	m Hexahydro-antolol	194 21	10945 7	10810 5	2105 1	2108 9	2105 9	37 1	2143 0	40

21	C ₇ H ₁₆ O	Allyl-methyl-ethyl-carbinol	114	11	9289	4	9199	3	1049	7	1051	4	1050	1	19.7	1069	8	21
22	C ₇ H ₁₆ O	<i>n</i> -Heptyl alcohol	116	13	9602	8	9599	7	1104	4	1106	4	1104	9	24	2	1129	1
23	C ₇ H ₁₆ O	Triethyl-carbinol	116	13	9385	4	9294	4	1079	4	1081	4	1080	0	20	0	1100	0
24	C ₈ H ₁₈ O	Diallyl-methyl-carbinol	126	11	9452	3	9360	6	1180	5	1182	2	1180	7	23	0	1203	7
25	C ₈ H ₁₈ O	1,3-Dimethyl-cyclohexanol-2	128	13	9421	9	9330	5	1195	5	1197	5	1196	0	25	7	1221	7
26	C ₈ H ₁₈ O	1,3-Dimethyl-cyclohexanol-5	128	13	9321	4	9231	0	1182	8	1184	8	1183	4	26	9	1210	3
27	C ₈ H ₁₈ O	Allyl-methylpropyl-carbinol	128	13	9408	8	9377	0	1201	5	1203	5	1201	9	22	9	1224	8
28	C ₈ H ₁₈ O	Allyl-diethyl-carbinol	128	13	9509	5	9417	3	1206	6	1208	6	1207	1	22	9	1230	0
29	C ₈ H ₁₈ O	1,3-Dimethyl-cyclohexanol-3	128	13	9394	1	9303	2	1192	0	1194	0	1192	5	26	6	1219	1
30	C ₈ H ₁₈ O	Methyl-1-cycloheptanol	128	13	9370	0	9279	1	1188	9	1190	9	1189	4	26	6	1216	0
31	C ₈ H ₁₈ O	Methyl-dipropyl-carbinol	130	14	9559	6	9466	9	1232	0	1234	4	1232	7	23	7	1256	4
32	C ₈ H ₁₈ O	1,3,5-Trimethyl-cyclohexene-6-ol-5	140	13	9327	9	9237	4	1294	4	1296	4	1294	7	30	0	1324	7
33	C ₈ H ₁₈ O	Methylethyl-1,3-cyclohexanol-3	142	14	9390	7	9299	6	1321	8	1324	1	1322	4	30	0	1352	4
34	C ₈ H ₁₈ O	Cycloheptyl-methyl-carbinol	142	14	9530	7	9438	3	1341	6	1343	9	1349	2	29	4	1371	6
35	C ₈ H ₁₈ O	<i>n</i> -Butylcarbinol	142	14	9692	4	9598	4	1364	3	1366	6	1364	9	27	7	1392	6
36	C ₈ H ₁₈ O	Allylmethyl <i>tert</i> -butylcarbinol	142	14	9679	1	9585	2	1362	4	1364	7	1363	0	26	1	1389	1
37	C ₈ H ₁₈ O	Ethyl-dipropyl-carbinol	144	16	9705	3	9611	2	1385	6	1388	2	1386	5	27	8	1414	3
38	C ₁₀ H ₁₈ O	Diallyl-propyl-carbinol	154	14	9640	7	9547	2	1471	6	1473	9	1472	1	31	2	1503	3
39	C ₁₀ H ₁₈ O	Allyl-dipropyl-carbinol	156	16	9811	1	9715	9	1517	2	1519	9	1518	0	31	3	1549	3
40	C ₁₁ H ₂₀ O	Allyl-methylhexyl-carbinol	170	18	9884	3	9788	4	1665	8	1668	7	1666	7	35	8	1702	5
41	C ₁₂ H ₂₂ O ₂	Dimethylol-cyclopropane	102	08	7002	4	6934	5	707	9	708	8	707	6	41

TABLE III — KETONES

No	Formula	Name	M	A_{un}	A_{cor} ($p=\text{const}$)	A_{mol} ($p=\text{const}$)	Δ_{mol} ($p=\text{const}$)	A_{mol} (obs) ($p=\text{const}$)	$W/19$	A_{gas} ($p=\text{const}$)	No
1	$\text{C}_4\text{H}_8\text{O}$	Methylethyl-ketone	72.06	8158	1 8079	0	582	1 583	3 9.8	592	1
2	$\text{C}_4\text{H}_8\text{O}$	Acetyl-trimethylene	84.06	8303	4 8222	9	691	2 692	4 11.5	702	2
3	$\text{C}_4\text{H}_{10}\text{O}$	Methylpropyl-ketone	86.08	8615	5 8531	9	734	4 736	5 11.5	746	3
4	$\text{C}_4\text{H}_{10}\text{O}$	Methyl-iso-propyl-ketone	86.08	8607	2 8523	7	733	7 734	9 11.0	744	4
5	$\text{C}_4\text{H}_{10}\text{O}$	Diethyl-ketone	86.08	8627	0 8543	3	735	4 736	6 11.7	747	5
6	$\text{C}_4\text{H}_{10}\text{O}$	β -Methyl-cyclopentanone	98.08	8578	6 8495	4	833	2 834	4 15.4	848	6
7	$\text{C}_4\text{H}_{10}\text{O}$	Acetyl-cyclobutane	98.08	8818	7 8733	2	856	6 857	8 14.9	871	7
8	$\text{C}_4\text{H}_{12}\text{O}$	Methylbutyl-ketone	100.10	9027	9 8940	3	894	9 896	4 14.2	909	8
9	$\text{C}_4\text{H}_{12}\text{O}$	<i>tert</i> -Methylbutyl-ketone	100.10	8993	5 8906	3	891	5 893	0 13.0	904	9
10	$\text{C}_4\text{H}_{12}\text{O}$	β -Methyl-cyclohexanone	112.10	8958	8 8871	9	994	5 996	0 18.9	1013	10
11	$\text{C}_4\text{H}_{12}\text{O}$	Cycloheptanone (Suberon)	112.10	8974	3 8887	2	996	3 997	8 19.9	1016	11
12	$\text{C}_4\text{H}_{12}\text{O}$	Ethyl-1-cyclopentanone-2	112.10	8918	8 8832	3	990	1 991	6 18.2	1008	12
13	$\text{C}_4\text{H}_{12}\text{O}$	1,3-Dimethyl-cyclopentanone-2	112.10	8913	1 8826	6	989	5 991	0 16.8	1006	13
14	$\text{C}_4\text{H}_{12}\text{O}$	Dipropyl-ketone	114.11	9293	3 9203	2	1050	2 1051	9 16.4	1066	14
15	$\text{C}_4\text{H}_{12}\text{O}$	1,3-Dimethyl-cyclohexene-6-one 5	124.10	8966	3 8879	3	1101	9 1103	4 24.2	1126	15
16	$\text{C}_4\text{H}_{12}\text{O}$	1,3-Dimethyl-cyclohexanone-2	126.11	9043	8 8956	1	1129	5 1131	2 20.7	1150	16
17	$\text{C}_4\text{H}_{12}\text{O}$	Methylhexyl-ketone	128.13	9494	3 9402	1	1204	7 1206	7 20.3	1225	17
18	$\text{C}_4\text{H}_{12}\text{O}$	1,1,5-Trimethyl-cyclohexene-5-one-3	138.11	9124	9 9036	4	1248	0 1249	7 24.2	1274.8	18
19	$\text{C}_4\text{H}_{12}\text{O}$	1,4-Methylacetyl-cyclohexanone	140.11	9134	1 9045	5	1267	4 1269	4 24.2	1292	19
20	$\text{C}_4\text{H}_{12}\text{O}$	Ethyl-cyclohexyl ketone	140.11	9290	8 9200	7	1289	1 1291	1 24.2	1313.7	20
21	$\text{C}_4\text{H}_{12}\text{O}$	Methyl-cycloheptyl-ketone	140.11	9209	9 9120	6	1277	9 1279	9 24.2	1302	21
22	$\text{C}_5\text{H}_{10}\text{O}$	Dihydrocarvone	152.11	9373	3 9282	4	1411	9 1413	9 29.7	1441.9	22
23	$\text{C}_5\text{H}_{10}\text{O}$	Carone	152.11	9271	1 9181	2	1396	6 1398	6 27.6	1424	23

TABLE IV.—ESTERS.

No.	Formula.	<i>M</i>	<i>A_{un}</i> (<i>p</i> -const)	<i>A_{cor}</i> (<i>p</i> -const)	<i>A_{mol}</i> (<i>p</i> -const)	<i>A_{mol}</i> (<i>p</i> -const)	<i>A_{mol}</i> (abs)	<i>W₁₈</i>	<i>A_{gas}</i>	No.
1	C ₄ H ₁₀ O ₄	90.05	3824.5	3787.4	341.1	341.1	340.8	10.8	351.6	1
2	C ₄ H ₈ O ₄	118.08	5340.9	5487.2	647.9	648.5	647.9	14.5	662.4	2
3	C ₄ H ₈ O ₄	114.08	7161.1	7091.6	809.0	809.9	809.1	15.8	824.9	3
4	C ₁₀ H ₁₆ O ₄	198.14	7468.7	7396.3	1465.5	1467.2	1465.8			4
5	C ₁₀ H ₁₆ O ₄	296.16	6291.0	6230.6	1845.3	1846.5	1844.9			5
6	C ₁₀ H ₁₆ O ₄	302.21	6485.3	6422.4	1940.9	1942.9	1941.1			6
7	C ₁₈ H ₃₀ O ₄	338.21	6892.8	6825.9	2308.6	2310.6	2308.6			7

Methyl ester of cyclobutane acid
Ethylester of methylethyl-1,4-cyclopentane acid

TABLE V.—ACIDS

No.	Formula.	<i>M</i>	<i>A_{un}</i> (<i>p</i> -const)	<i>A_{cor}</i> (<i>p</i> -const)	<i>A_{mol}</i> (<i>p</i> -const)	<i>A_{mol}</i> (<i>p</i> -const)	<i>A_{mol}</i> (abs)	<i>W₁₈</i>	<i>A_{gas}</i>	No.
1	C ₄ H ₈ O ₄	86.05	5877.6	5822.3	483.8	484.1	483.7	17.3	501.0	1
2	C ₄ H ₈ O ₄	100.06	6450.8	6388.3	639.2	639.8	639.2	19.9	659.1	2
3	C ₄ H ₈ O ₄	116.10	7225.6	7153.3	830.8	832.0	831.0	21.5	852.5	3
4	C ₄ H ₈ O ₄	116.10	7226.6	7156.5	830.9	832.1	831.1	21.5	852.6	4
5	C ₇ H ₁₂ O ₄	128.10	7361.4	7290.0	933.8	935.0	934.0			5
6	C ₄ H ₈ O ₄	142.11	7715.5	7640.7	1085.8	1087.3	1086.2			6
7	C ₄ H ₈ O ₄	142.11	7736.9	7661.9	1088.8	1090.3	1089.2			7
8	C ₄ H ₈ O ₄	142.11	7683.9	7609.4	1081.4	1082.9	1081.8			8
9	C ₄ H ₈ O ₄	142.11	7720.3	7645.4	1086.5	1088.0	1087.9			9

Trimethylene-carbon acid
Cyclobutane-carbon acid
Capric acid (act)
Acid from the chloride of russian benzene
Cyclohexane-carbon acid
Hexahydro-*m*-tolyl acid
Cyclo-octane acid (act)
Acid from benzene, 100-102°
Cycloheptane-carbon acid

TABLE VI.—NITROGEN CONTAINING SUBSTANCES

No.	Formula.	<i>M</i>	<i>A_{un}</i> (<i>p</i> -const)	<i>A_{cor}</i> (<i>p</i> -const)	<i>A_{mol}</i> (<i>p</i> -const)	<i>A_{mol}</i> (<i>p</i> -const)	<i>A_{mol}</i> (abs)	<i>W₁₈</i>	<i>A_{gas}</i>	No.
1	C ₄ H ₁₀ ON	87.08	7497.5	7424.8	646.6	647.3	646.5	17.5	664.0	1
2	C ₄ H ₁₀ ON	135.15	8873.1	8787.0	1363.3	1365.2	1363.5			2
3	C ₄ H ₁₂ N	85.10	9767.2	9672.5	823.1	824.4	823.1	11.1	834.4	3
4	C ₇ H ₁₂ N	113.13	9982.0	9885.2	1118.3	1120.2	1118.7	16.8	1135.5	4
5	C ₄ H ₁₂ N	141.16	10213.6	10114.5	1427.8	1430.3	1428.4	22.1	1450.5	5
6	C ₄ H ₁₂ N	100.10	9059.2	8971.3	898.0	899.5	898.5	11.7	910.2	6

Methylethyl-ketoxime
Cyclo-heptylmethyl-ketoxime
1,1-Amino-cyclopropyl-ethane
1-Methyl-cyclohexyl-amine-3
Cycloheptyl-methylamino-methane
Dimethyl-4,4-tetrahydro-furane

at t° . Where the experimental data for this computation were not known, the values for W'_{18} were interpolated. A_{gas} indicates the molecular heat of combustion of the substances in the gaseous state at t° and $p = \text{const.}$

A comparison of Zubow's data with those of other authors will be made in the next paper.

WARSAW, POLAND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE CRYSTAL STRUCTURE OF CESIUM DICHLORO-IODIDE.¹

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Purpose of the Investigation.—The crystal structure of the alkali halides, sodium and potassium chlorides, has been determined.² It has seemed of particular interest to ascertain the modifications in this structure which result when more halogen atoms are introduced into the molecule with the formation of alkali polyhalides.

The real nature of these compounds has long been in doubt and it was felt that a knowledge of the crystal structure of a typical polyhalide might aid in removing this uncertainty. Formerly it was customary to consider these compounds as "double salts" or "addition compounds," for instance the trihalides as compounds of RX and $XX'(CsCl \cdot ICl)$ where R is an alkali metal and X and X' are halogens, and the pentahalides as compounds of RX and $XX'_3(CsCl \cdot ICl_3)$.³ The ease with which such compounds as $R(ICl_4)$ are decomposed into normal halide and complex halogen (RCl and ICl_3) by carbon tetrachloride⁴ supported this view. By some the halogen atoms were considered to be grouped about the positive atom but as Werner⁵ has pointed out, this point of view is quite untenable. The view which seems to agree best with the properties of these compounds considers them to be compounds of metal ion or group and complex halogen anion.⁶ More recent studies, especially upon the polyiodides, have strengthened this view.⁶

Cesium dichloro-iodide ($CsCl_2I$) was chosen for this study of crystal structure because of its supposed dimorphism, and because experience had shown that good crystals of one of these forms at least could be readily prepared.

¹ This article is based upon a portion of the thesis presented to the Faculty of the Graduate School of Cornell University by Ralph W. G. Wyckoff in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," 1918. Chap. VII.

³ Wells and Penfield, *Am. J. Sci.*, [3] 43, 29 (1892) discuss possible structures for the trihalides.

⁴ Weinland and Schlegelmilch, *Z. anorg. Chem.*, 30, 134 (1902).

⁵ A. Werner, "New Ideas on Inorganic Chemistry" (Hedley, translator), 1911, p. 86.

⁶ R. Abegg u. F. Auerbach, "Handbuch d. anorg. Chem.," Bd. IV, *Abt.*, 2, 432 et seq. (1913).

Preparation of the Specimens.—Cesium dichloro-iodide is described as crystallizing in 2 forms, a hexagonal and a rhombic modification. The hexagonal cesium dichloro-iodide is obtained from solutions which are rather weak in cesium chloride (CsCl). If cesium chloride is present in larger quantities, the rhombic form is said to result.¹

Rhombohedral (hexagonal) cesium dichloro-iodide was obtained by dissolving about 10 g. of cesium chloride in 50 cc. of water, adding 8 g. of iodine, and passing chlorine through the hot solution until all the iodine had dissolved.² Six-sided plates (less than a millimeter in thickness, but nearly a centimeter in diameter) formed upon slow cooling. The edges of these plates reflect light well but the 2 large faces are invariably dull and pitted.

All attempts to prepare the rhombic modification by increasing the amount of cesium chloride failed. When the concentration recommended by Wells and Penfield² was used, small crystals that were apparently of the rhombic system appeared. But when these crystals were examined by the X-rays the pattern that was obtained clearly indicated that the crystals were not simple, but twinned. On breaking the crystals they were frequently found to be hollow. Usually all of the faces appearing upon these crystals reflected light fairly well. Attempts to grow rhombic crystals by slow evaporation over sulfuric acid in a room of constant temperature also failed. Under these conditions twined crystals were always obtained. Crystals were grown from solutions, the cesium chloride content of which varied by small steps from a solution containing one molecule of cesium chloride to 5 molecules of water, from which rhombohedral plates of cesium dichloro-iodide were obtained, to the point where cesium chloride itself crystallized out.

Because of the failure to produce true rhombic cesium dichloro-iodide the special rhombohedral arrangement, which shows only in this particular polyhalide, has alone been determined.

The cesium chloride used in preparing the cesium dichloro-iodide was very pure. It was originally obtained from pollucite, and an arc spectrum photograph showed the presence of no other alkalis.

The Method of Crystal Structure Determination.—The method of study is similar to that used by Nishikawa in studying the structure of the spinels.⁴ This method may be considered as made up of 2 parts.

1. The study of the X-ray spectrum obtained from the anticathode of an X-ray bulb using the crystal under investigation as a grating. From

¹ Wells and Penfield, *loc. cit.*, p. 17.

² If an excess of chlorine is used, cesium tetrachloro-iodide (CsCl_4I) is produced (Wells and Penfield, *loc. cit.*).

³ *Loc. cit.*

⁴ S. Nishikawa, *Tokyo Sugaku-Bunrigakkaishi Kisi*, [2] 8, 199 (1915).

this spectrum the distance between like planes in the crystal can be ascertained and information can be obtained concerning the kind of unit which by repetition of itself builds up the crystal.

2 The study of the Laue patterns obtained by passing X-rays through a section of the crystal.

Part 1. The Study of the X-ray Spectrum.—The X-ray spectrum of tungsten from a Coolidge tube was obtained by reflection from the large (111) face of a crystal. The distances measured upon the photographic plate from the image of the slit to the principal tungsten lines are:

Line	Wave Length ^a Å U	Plate Distance Cm.
α_1	1 475	8 6
β_1	1 278	6 9
β_2	1 241	6 7
γ_1	1 095	5 6

^a M. Siegbahn, *Jahrb. Radioakt. Elektronik*, [3] 13, 296 (1916)

The order of the spectrum which appears upon the plate is not known. But from the above data the value of the ratio d/n (where d is the distance between like planes of this face and n is the order of the spectrum) can be calculated. The well-known expression, $n\lambda = 2d \sin \theta$, where n and d have the meanings already given, $\lambda =$ the wave length of the X-rays, $\theta =$ the angle of the reflection,¹ holds in this case. From this equation $d/n = \lambda/(2 \sin \theta)$ results. The distances measured upon the photographic plate from the particular lines to the position of zero deflection are equal to the distances from the crystal to the plate (9.25 cm. approximately) multiplied by the $\tan 2\theta$. Calculations from the above data lead to the following values for d/n .

Line	d/n .
α_1	2.01
β_1	2.015
β_2	2.01
γ_1	2.03

A more accurate determination of this ratio can be made, using the reference spectrum from sodium chloride. In making this comparison spectrum, crystals of cesium dichloro-iodide and sodium chloride were mounted together, one above the other. The spacing for sodium chloride is accurately known² so that by the use of this sodium chloride spectrum it is possible to get the distance from the crystal to the plate with greater accuracy. The following table gives measurements upon this second photograph:

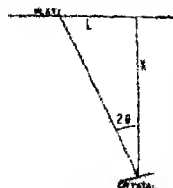


Fig. 1.

¹ W. H. Bragg and W. L. Bragg, *loc. cit.*, Chap. II.

² W. H. Bragg and W. L. Bragg, *ibid.*, p. 71.

Line	Distance upon the plate from slit image to line for		Wave Length Å U.
	NaCl Cm	CsCl ₂ I Cm	
α_1	5.55	8.65	1.471
β_4	4.75	7.20	1.296
β_1	4.68	7.05	1.278
β_3	4.58	6.90	1.258
β_2	4.50	6.75	1.241
γ_1	3.92	5.75	1.095

The distance from the crystal to the plate, z , is given by $\sin \theta = n\lambda/2d$, $\tan 2\theta = m/z$ or $z = m/\tan 2\theta$, where m is the distance of the spectrum line from the undeviated line. This leads to the following values for x

Line	Cm
α_1	9.44
β_4	9.43
β_1	9.44
β_3	9.47
β_2	9.4
γ_1	9.43
	9.44

This value of z , when used for the more accurate evaluation of d/n for cesium dichloro-iodide leads to

Line	d/n
α_1	2.03
β_4	2.02
β_1	2.03
β_3	2.02
β_2	2.03
γ_1	2.02
	2.02×10^{-8} cm

The Density of Cesium Dichloro-iodide.—In order to know the number of molecules associated with the unit of structure and the shape of this unit, the density of the salt must be known. As no determinations were to be found in the literature, the following measurements were made. Great accuracy in this determination was not needed for the present purpose. The density was found by observing the buoyant effect of benzene upon definite weights of cesium dichloro-iodide. Most of the air could be removed from the particles of the solid by keeping the salt during the determination in a small bottle which could be placed in boiling benzene. A number of determinations gave a mean density for cesium dichloro-iodide of 3.86.

The Unit of Structure. Cesium dichloro-iodide belongs to the rhombohedral division of the hexagonal system. Two lattices, or units of struc-

ture, are fundamental to this division—the hexagonal lattice (Γ_h) and the rhombohedral lattice (Γ_r).¹ The spacing (d) between like planes of either of these units can be obtained in terms of the crystallographic data, the density (ρ), the weight of one molecule of the salt (M), the number of molecules associated with the unit of structure (m), and the order of the reflection spectrum (n). In the case of the rhombohedral unit (Γ_r)

$$V = \frac{c^3}{3\sqrt{3}} \frac{1 - \cos \alpha}{1 + 2 \cos \alpha},$$

where c = the body diagonal of the unit, α = the angle between the rhombohedral axes, and V = the volume of the unit rhombohedron.

$$c = \sqrt[3]{V \frac{1 + 2 \cos \alpha}{1 - \cos \alpha}},$$

$$d = c/3 = \frac{1}{\sqrt{3}} \sqrt[3]{V \frac{1 + 2 \cos \alpha}{1 - \cos \alpha}}, \quad V = mM/\rho$$

$$d^3 = \frac{mM (1 + 2 \cos \alpha)}{3\sqrt{3} \rho (1 - \cos \alpha)},$$

$$d^3/n^3 = \frac{M (1 + 2 \cos \alpha) m}{3\sqrt{3} \rho (1 - \cos \alpha) n^3},$$

$$n^3/m = \frac{M}{\rho \times (d/n)^3 \times 3\sqrt{3}} \times \frac{1 + 2 \cos \alpha}{1 - \cos \alpha}.$$

$M = 330.7 \times 1.64 \times 10^{-24}$ g, where 1.64×10^{-24} g. is the weight of one atom of hydrogen.²

$$\rho = 3.86$$

$$\alpha = 98^\circ 22'.$$

$$d/n = 2.03 \times 10^{-8} \text{ cm.}$$

$$n^3/m = 2.001.$$

Since n , the order of the spectrum, is not known with certainty, the number of molecules associated with the unit cell cannot be evaluated directly. The value of n^3/m , however, is seen to agree very closely with the value it would have if 4 molecules were associated with the unit of structure and the reflection were of the second order. A consideration of the other possible unit, the hexagonal prism, makes Γ_h seem highly improbable as the fundamental lattice for cesium dichloro-iodide. The results from these spectra measurements point then to a rhombohedral unit containing 4 molecules. The later study of the Laue photographs confirms this conclusion.

The value of m or m_1 , the number of molecules associated with the unit of structure cannot be told directly because n cannot be evaluated

¹ A. Schönflies, "Krystallsysteme und Krystallstruktur," p. 459.

² W. H. Bragg and W. L. Bragg, *loc. cit.*, p. 110.

³ F. Groth, "Chemische Krystallographie," 2, 305 (1906).

with certainty. It can, however, be obtained in the following indirect fashion. All possible values of the ratio n^3/m are shown in the following table:

m	1	2	3	4	6	12
n						
1	1	0.50	0.33	0.25	0.16	0.08
2	8	4.00	2.67	2.00	1.33	0.67
3	27	13.50	9.00	6.75	4.50	2.25
4	64	32.00	21.33	16.00	10.67	5.33

From an inspection of this table it is evident that 4 molecules are associated with the unit cell, which is a rhombohedron. The spectrum obtained upon the photographic plate is of the second order.

Part 2. The Study of the Laue Patterns.—A symmetrical Laue photograph made by passing the X-rays in a direction normal to the (111) face of a crystal and several unsymmetrical photographs when the rays were not exactly perpendicular to this face were prepared. Stereographic projections of these photographs were made and the indices of the planes producing the various spots in the figures were determined. The manner of drawing this projection is given by the following data for the symmetrical case (Fig. 1a).

XYZ is the plane of the photographic plate,

O is the position of the crystal,

$XZ = XY = YZ$,

$OI = 5$ cm., $YXI = 30^\circ$,

$b \sin \alpha/2 = 1/2 XY = x \cos 30^\circ = x\sqrt{3}/2$,

therefore

$$b = \frac{x\sqrt{3}}{2 \sin \alpha/2}.$$

Also

$$x^2 + 5^2 = \frac{3x^2}{4 \sin^2 \alpha/2}, \text{ and } x = 8.98 \text{ cm.}$$

If an attempt is made to construct the diagram using a base built upon this value of x , there is no simple correspondence between the calculated and observed positions of the spots. This agreement, however, is obtained by taking as axes the face diagonals of the figure (as z). These new axes rather than the old are to be considered as the axes of the unit rhombohedron. The necessary calculations follow:

$$x \sin 30^\circ = u,$$

$$x^2 = 5^2 + u^2,$$

$$z = \sqrt{5^2 + [8.98 \sin 30^\circ]^2} = 6.72 \text{ cm.}$$

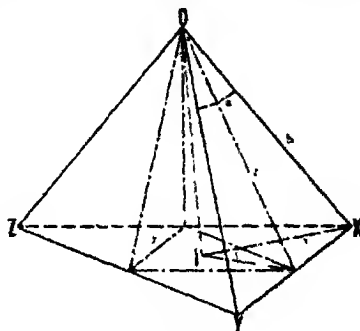


Fig. 1a.

$$y = x \cos 30^\circ = 7.77 \text{ cm.},$$

$$\beta \text{ (the new face angle)} = \sin^{-1} (y/2)/z \times 2 = 70^\circ 42',$$



Fig. 2

The distance¹ between a plane (hkl) and a parallel plane through a point (x_1, y_1, z_1) in a rhombohedral lattice is

$$\frac{(hx_1 + ky_1 + lz_1 - 1) \sqrt{1 + \cos^2 \beta - 3 \cos^2 \beta}}{\sqrt{(h^2 + k^2 + l^2) \sin^2 \beta + 2(hk + hl + kl) (\cos^2 \beta - \cos \beta)}}$$

where h, k, l are the Miller indices of the plane. β , the angle between

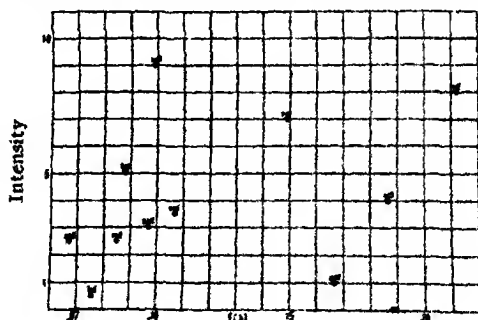


Fig. 3.

the crystallographic axes, $= 70^\circ 42'$. x_1, y_1, z_1 are the coordinates of the point of reference. From this d (the spacing) is seen to vary with

$$\frac{1}{\sqrt{(h^2 + k^2 + l^2) \sin^2 \beta + 2(hk + hl + kl) (\cos^2 \beta - \cos \beta)}}$$

But $d = \frac{n\lambda}{2 \sin \theta}$, consequently $\frac{n\lambda}{2 \sin \theta}$ varies with the value of the

¹ A. W. Hull, *Phys. Rev.*, [2] 10, 661 (1917).

above expression and the wave length, λ , of the X-rays producing a spot is a function of

$$\frac{\sin \theta}{\sqrt{h^2 + k^2 + l^2} \sin^2 \beta + 2(hk + hl + kl) (\cos^2 \beta - \cos \beta)} = f(\lambda).$$

The distance of a spot from the undeviated position, as measured upon the photographic plate, divided by the distance from the crystal to the plate is the tangent of twice the angle of reflection, θ . The relative intensities given in the following tables are from estimations made upon

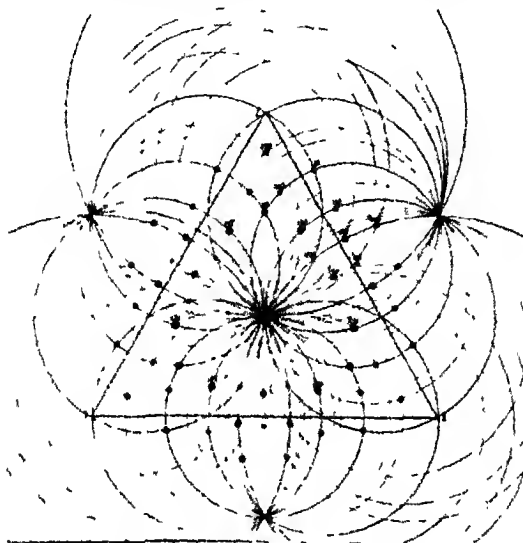


Fig. 4.

the negative. The value of $f(\lambda)$ for the various spots which appear are plotted against intensities in Fig. 3. The stereographic projection of this symmetrical photograph (Fig. 2) is shown in Fig. 4.

TABLE I—DATA FROM THE SYMMETRICAL LAUE PHOTOGRAPH

hkl	Distance from central spot	$f(\lambda)$	Intensity.
$02\bar{1}$	1.90	0.3330	1.0
$11\bar{1}$	2.65	0.424	8.0
$12\bar{1}$	4.03	0.373	4.0
$03\bar{1}$	2.80	0.298	7.0
$05\bar{1}$	3.75	0.214	3.5
$13\bar{2}$	2.30	0.198	9.0
$\bar{1}4\bar{1}$	1.95	0.177	5.0
$\bar{1}6\bar{1}$	2.85	0.152	0.5
$15\bar{2}$	3.40	0.170	2.5
$33\bar{2}$	4.30	0.193	3.0
$34\bar{3}$	3.15	0.134	2.5

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Similar measurements were made upon 3 unsymmetrical photographs and the data thus obtained are contained in the accompanying Tables (II, III and IV). In all cases the distance from the crystal to the photographic plate was 5 cm.

TABLE II.—DATA FROM THE FIRST UNSYMMETRICAL LAUE PHOTOGRAPH.

hkl	Distance from central spot.	$f(\lambda)$	Intensity.
021	1.40	0.0592	2.5
120	1.15	0.0492	2.0
102	1.50	0.0630	2.0
012	1.95	0.0805	3.5
210	2.53	0.1000	6.0
201	2.35	0.0948	5.5
111	2.50	0.131	5.5
111	3.15	0.158	2.0
111	1.78	0.103	8.0
121	3.72	0.131	2.0
121	3.05	0.113	3.0
112	3.25	0.118	2.7
112	4.55	0.150	0.5
211	5.10	0.161	0.2
211	4.4	0.147	0.5
031	2.25	0.066	6.5
130	2.10	0.062	7.0
103	2.50	0.072	3.0
013	2.95	0.093	1.0
310	3.60	0.096	0.7
301	3.40	0.092	0.7
051	3.10	0.0545	5.5
150	2.95	0.0526	6.0
105	3.50	0.0588	2.5
015	3.75	0.0628	2.0
510	4.70	0.0780	0.4
501	4.60	0.0800	0.4
132	2.00	0.0495	8.0
231	1.55	0.0393	4.0
213	1.75	0.0437	7.0
123	2.60	0.0624	3.5
321	3.00	0.0700	3.0
312	2.60	0.0624	3.5
141	1.35	0.0304	0.5
114	1.85	0.0404	2.5
411	2.60	0.0547	4.5
116	2.5 ^{ab}	0.0372	0.1
611	3.65	0.0498	2.5
152	2.90	0.0480	4.0
251	2.55	0.0430	4.0
215	2.90	0.0480	3.7
125	3.65	0.0568	1.0
521	4.30	0.0639	0.5
512	3.95	0.0603	0.7

TABLE II (continued)

hkl	Distance from central spot	$f(\lambda)$	Intensity.
$3\bar{3}2$	3 40	0 0641	1 5
$2\bar{3}3$			
$3\bar{2}3$	4 30	0 0762	0 3
$2\bar{3}3$			
$3\bar{2}3$	2 25	0 0434	4 2
$2\bar{3}3$	2 35	0 0451	4 5
$3\bar{3}2$	2 10	0 0407	0 1
$1\bar{4}3$	1 30	0 0241	0 1
$1\bar{3}4$	2 00	0 0359	0 2
$4\bar{3}1$	2 30	0 0406	0 6
$3\bar{4}3$	2 8 ±	0 0435	0 2
$3\bar{3}4$	3 70	0 0536	2 0
$3\bar{3}4$	3 85	0 0552	2 0
$4\bar{3}3$	3 30	0 0492	3 0
$4\bar{3}3$	3 00	0 0457	3 0
$2\bar{5}3$	2 70	0 0395	0 2
$3\bar{5}2$	2 15	0 0446	0 1
$2\bar{3}5$	3 30	0 0463	2 0
$5\bar{3}2$	3 70	0 0505	2 5
$5\bar{2}3$	3 25	0 0458	2 0

TABLE III - DATA FROM THE SECOND UNSYMMETRICAL LAUE PHOTOGRAPH

hkl	Distance from central spot	$f(\lambda)$	Intensity
010	6 75	0 342	7 0
$\bar{1}01$	3 25	0 109	20 0
$\bar{1}20$	2 55	0 0547	3 0
$\bar{1}02$	7 15	0 147	4 0
$\bar{1}30$	3 80	0 0597	8 5
$\bar{1}03$	9 05	0 130	3 3
031	2 30	0 0359	7 0
041	3 35	0 0406	0 5
$\bar{1}40$	4 50	0 0544	0 2
051	3 90	0 0384	6 0
$\bar{1}50$	4 90	0 0477	8 0
$\bar{1}05$	10 85	0 095	1 5
061	4 35	0 0361	0 8
$\bar{1}60$	5 22	0 0431	1 4
071	4 80	0 0400	0 3
$\bar{1}70$	5 42	0 0377	1 1
$\bar{1}07$	11 65	0 0724	0 2
140	9 07	0 1134	1 2
150	8 63	0 0852	3 5
170	8 10	0 0589	3 0
710	8 95	0 0635	3 0
190	7 80	0 0442	1 0
910	8 50	0 0474	0 9
$\bar{3}41$	3 20	0 0299	0 8
$\bar{6}31$	4 25	0 0305	0 1

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TABLE III (continued)

hkl	Distance from central spot	$f(\lambda)$	Intensity.
$\bar{2}11$	1 85	0 0349	15 0
$\bar{2}21$	3 54	0 0561	0 5
$\bar{2}31$	4 47	0 0582	7 0
$\bar{2}51$	5 44	0 0483	7 2
$\bar{2}61$	5 70	0 0437	1 0
$\bar{2}71$	5 88	0 0393	1 0
$\bar{2}12$	5 15	0 081	1 5
$\bar{2}13$	7 35	0 0913	4 0
$\bar{2}15$	9 80	0 0806	3 8
$\bar{3}12$	2 40	0 0306	6 0
$\bar{3}13$	4 60	0 0500	0 2
$\bar{3}14$	6 15	0 0560	5 6
$\bar{3}16$	8 25	0 0558	2 5
$\bar{2}03$	5 63	0 0723	0 1
$\bar{2}2\bar{1}$	4 87	0 0852	6 0
$\bar{2}3\bar{1}$	5 85	0 0768	7 5
$\bar{2}4\bar{1}$	6 30	0 0716	2 0
$\bar{2}5\bar{1}$	6 58	0 0627	7 0
$\bar{2}7\bar{1}$	6 75	0 0477	3 0
$\bar{1}2\bar{1}$	3 10	0 0892	9 0
$\bar{1}3\bar{1}$	4 30	0 0670	2 2
$\bar{1}4\bar{1}$	4 95	0 0600	8 5
$\bar{1}5\bar{1}$	5 32	0 0525	1 8
$\bar{1}6\bar{1}$	5 55	0 0462	6 0
$\bar{3}3\bar{2}$	3 30	0 0358	4 5
$\bar{3}4\bar{2}$	4 15	0 0399	0 2
$\bar{3}5\bar{2}$	4 75	0 0402	4 0
$\bar{5}5\bar{2}$	6 00	0 0129	3 5
$\bar{5}7\bar{2}$	6 70	0 0371	0 1
$\bar{3}3\bar{1}$	6 85	0 0825	2 7
$\bar{3}4\bar{1}$	7 35	0 0761	6 3
$\bar{3}6\bar{1}$	7 68	0 0594	4 3
$\bar{3}8\bar{1}$	7 70	0 0467	3 5
$\bar{4}5\bar{1}$	8 30	0 0669	5 0
$\bar{4}7\bar{1}$	8 45	0 0549	3 0
$\bar{5}6\bar{1}$	8 38	0 057	3 5
$\bar{5}8\bar{1}$	9 00	0 0499	1 0
$\bar{3}22$	3 68	0 0421	0 3
$\bar{3}32$	4 55	0 0464	6 5
$\bar{3}52$	5 63	0 044	4 5
$\bar{3}23$	5 65	0 0565	6 0
$\bar{1}11$	6 45	0 175	3 5
$\bar{3}43$	6 97	0 0568	3 2
$\bar{2}32$	7 16	0 0800	0 1
$\bar{3}53$	7 28	0 0530	0 1
$\bar{1}21$	7 50	0 147	6 0
$\bar{2}52$	7 60	0 0641	0 1
$\bar{1}31$	7.63	0 113	4 0
$\bar{1}41$	7.60	0.0885	4 5

TABLE III (continued)

hkl	Distance from central spot	$f(\lambda)$	Intensity
$\bar{1}31$	7.52	0.0716	0.3
$\bar{1}61$	7.48	0.0602	4.5
$\bar{1}81$	7.32	0.0449	0.5
$\bar{4}15$	5.50	0.0397	0.2
$\bar{4}35$	7.10	0.0470	2.0
$\bar{4}55$	8.00	0.0465	0.2
$\bar{3}14$	3.60	0.0335	0.5
$\bar{3}34$	7.95	0.0638	4.5
$\bar{3}54$	8.70	0.0583	1.5
$21\bar{3}$	3.70	0.0470	20.0
$23\bar{3}$	9.25	0.0917	3.4
$\bar{3}45$	9.60	0.0629	1.0
325	8.37	0.0629	4.0
$\bar{1}12$	10.05	0.187	3.3
305	6.20	0.0514	5.5
102	7.15	0.147	4.5
$\bar{3}07$	7.75	0.0466	1.5
103	9.00	0.129	3.5
105	10.85	0.0948	2.8
316	6.00	0.0497	0.5
215	6.65	0.0678	4.0
$\bar{2}17$	8.25	0.0512	2.5
$\bar{1}\bar{1}2$	3.80	0.074	13.0
$\bar{1}13$	6.10	0.085	1.5
$\bar{1}\bar{1}4$	7.65	0.0835	4.5
$\bar{1}\bar{1}6$	9.30	0.0679	4.0

TABLE IV - DATA FROM THE THIRD UNSYMMETRICAL LAUE PHOTOGRAPH.

hkl	Distance from central spot	$f(\lambda)$	Intensity.
$52\bar{3}$	3.61	0.0495	1.0
$43\bar{3}$	3.37	0.0550	1.8
$31\bar{2}$	2.95	0.0693	1.5
$41\bar{7}$	2.30	0.0401	0.5
$32\bar{3}$	2.00	0.0388	0.5
$11\bar{1}$	2.50	0.1305	2.5
$34\bar{3}$	2.90	0.0446	1.5
121	3.30	0.1195	2.0
$13\bar{1}$	3.55	0.0946	1.0
$14\bar{1}$	3.62	0.0760	1.0
$16\bar{1}$	3.70	0.0535	1.0
010	3.55	0.3210	2.0
$\bar{1}61$	3.05	0.0465	1.8
$\bar{1}41$	2.80	0.0628	3.5
$15\bar{2}$	2.25	0.0335	0.6
$05\bar{1}$	2.20	0.0408	3.5
$13\bar{2}$	1.58	0.0399	3.0
$03\bar{1}$	1.50	0.0455	8.0
$\bar{1}30$	1.15	0.0355	2.0

TABLE IV (continued).

hkl .	Distance from central spot.	$f(\lambda)$.	Intensity.
$\bar{1}11$	0.95	0 0528	2.5
$\bar{2}13$	1.20	0 0310	1.5
$\bar{1}02$	1.20	0 0513	1.5
$\bar{1}21$	2.00	0 0782	3.2
$\bar{2}53$	3.05	0 0464	2.0
$\bar{2}33$	2.40	0 0485	5.0
$\bar{1}22$	3.40	0 1035	1.5
$\bar{2}35$	3.55	0 0518	2.0
$\bar{2}15$	2.45	0 0414	3.0
$\bar{1}13$	3.40	0 0915	1.0
$\bar{1}05$	3.30	0 0569	2.0
$\bar{1}03$	2.30	0 0671	4.0
$\bar{1}14$	1.85	0 0404	2.0
$0\bar{1}1$	0.72	0 0482	20.0
$0\bar{1}2$	2.30	0 0929	4.5
$0\bar{1}3$	3.15	0 0870	1.5
$0\bar{1}5$	4.00	0 0657	1.0
$1\bar{3}2$	1.20	0 0310	1.8
$1\bar{2}1$	1.28	0 0485	15.0
$2\bar{3}1$	1.45	0 0358	1.5
$1\bar{3}4$	2.45	0 0429	2.2
$1\bar{2}5$	4.20	0 0626	1.0
$1\bar{2}3$	3.30	0 0754	1.0
$2\bar{3}5$	4.10	0 0542	0.5
$2\bar{3}3$	3.05	0 0559	1.6
$3\bar{4}3$	2.75	0 0417	0.7
$3\bar{3}2$	3.35	0 0599	1.4
$2\bar{2}1$	2.90	0 1070	0.5
$1\bar{1}0$	1.55	0 1010	15.0
$4\bar{3}1$	3.35	0 0549	1.0
$3\bar{2}1$	1.50	0 0364	2.0
$5\bar{3}0$	3.10	0 0452	1.0
$2\bar{1}0$	3.70	0 136	0.7
$5\bar{2}1$	3.10	0 0482	1.0
$4\bar{1}1$	3.60	0 070	10.0
$2\bar{1}1$	1.35	0 0512	15.0
$3\bar{1}2$	1.20	0 0300	2.0
$5\bar{1}2$	2.80	0 0447	1.5
$20\bar{1}$	3.05	0 1175	1.8

Calculations from the Laue Photographs.—The symmetry of cesium dichloro-iodide is that of the point group D_3^d .¹ The spectrum measurements indicate that the fundamental lattice is Γ_{rh} . There are 2 groups of D_3^d which have Γ_{rh} as the lattice, D_{3d}^5 and D_{3d}^6 . The fact that planes having two odd and one even indices are effective in the first order shows that the cell must be body-centered. The simplest body-centered cell which possesses the new face diagonal axes contains one molecule. The

¹ A. Schonflies, *loc. cit.*, pp. 95, 475.

arrangement of the atoms within a unit rhombohedron containing one molecule of cesium dichloro-iodide is shown in Fig. 5, the cesium atom being placed at the origin, the iodine atom in the center and the 2 chlorine atoms along the diagonal joining them. This arrangement may be considered as a special case of D_{3d}^5 . The coördinates of these points will be: Cs (0, 0, 0); I ($a/2$, $a/2$, $a/2$); Cl (α/a , α/a , α/a); ($-\alpha/a$, $-\alpha/a$, $-\alpha/a$); where α/a is some fractional part of a , the length of a side of the rhombohedron.

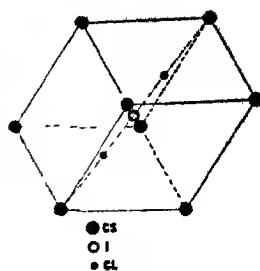


Fig. 5.

Assuming this arrangement for the atoms in the unit of structure for cesium dichloro-iodide, the intensity of reflection of the X-rays from any plane can be considered as proportional to the sum of the squares of 2 terms:

$$A^2 + B^2 \propto \text{Intensity.}$$

$$A = \text{Cs} \cos 2\pi n(hx + ky + lz) + \text{I} \cos 2\pi n(hx_1 + ky_1 + lz_1) + \text{Cl} \cos 2\pi n(hx_2 + ky_2 + lz_2) + \text{Cl} \cos 2\pi n(hx_3 + ky_3 + lz_3).$$

$$B = \text{Cs} \sin 2\pi n(hx + ky + lz) + \text{I} \sin 2\pi n(hx_1 + ky_1 + lz_1) + \text{Cl} \sin 2\pi n(hx_2 + ky_2 + lz_2) + \text{Cl} \sin 2\pi n(hx_3 + ky_3 + lz_3),$$

where n is the order of the reflection, hkl are the Miller indices of the reflecting plane, $x_n y_n z_n$ are the coördinates of the various atoms in the unit, and Cs, I and Cl represent the atomic numbers (or atomic weights) of these elements.

Introducing the values for $x_n y_n z_n$, these become

$$A = \text{Cs} \cos 2\pi n(0) + \text{I} \cos \pi n(h + k + l) + 2\text{Cl} \cos 2\pi n\alpha/a(h + k + l),$$

$$B = \text{Cs} \sin 2\pi n(0) + \text{I} \sin \pi n(h + k + l) + 0;$$

and these immediately reduce to

$$A = \text{Cs} + \text{I} + 2\text{Cl} \cos 2\pi n\alpha/a(h + k + l),$$

$$B = 0.$$

Two general cases arise when $n = 1$:

(1) When $(h + k + l)$ is odd.

$$A = \text{Cs} - \text{I} + 2\text{Cl} \cos 2\pi \alpha/a(h + k + l).$$

Because cesium and iodine would be expected to have about the same diffracting power, the chlorine atoms should be very effective. This will be the case with points having either all odd or 2 even and one odd indices.

(2) When $(h + k + l)$ is even.

$$A = \text{Cs} + \text{I} + 2\text{Cl} \cos 2\pi \alpha/a(h + k + l).$$

Points having 2 odd and one even indices fall in this class.

If $n = 2$ the effects of the cesium and iodine atoms will always add together.

To Determine the Position of Chlorine.—A few points will be found in the first order which do not have 2 odd and one even indices. These points fall into 3 groups according to the value of $(h + k + l)$.

$$(h + k + l) = 1. \quad \bar{3}22, \bar{1}20, \bar{1}11, \bar{3}13, \bar{2}21.$$

$$= 3. \quad 04\bar{1}, 13\bar{1}.$$

$$= 5. \quad 34\bar{2}, \bar{2}61, \bar{1}60, \bar{3}53, \bar{2}52, \bar{1}51, 140.$$

They should be especially effective for the placing of chlorine because it is to be expected that cesium and iodine will practically neutralize one another.

If various values are assigned to α/a in the preceding equations, there will be changes in A (the amplitude of the reflected beam) which can be represented by the series of curves of Fig. 6.

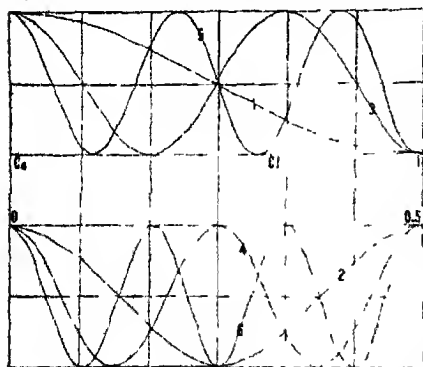


Fig 6

the constant value of $Cs - I$ has been neglected. The system of curves is thus symmetrical about its center point and consequently information derived from these curves will not be sufficient to settle between 2 possible positions of the chlorine atoms. In one of these positions the chlorine atoms will lie closer to the iodine atom than to the cesium atom; in the other this condition will be reversed. It will be assumed for the purposes

of calculation that the chlorine atoms lie closer to the iodine atom than to the cesium atom. If this is the case the curves show that the chlorine atoms must lie between $\alpha/a = 0.3$ and $\alpha/a = 0.4$ and between $\alpha/a = 0.6$ and $\alpha/a = 0.7$.

In one photograph the 2 points $05\bar{1}$ and $1\bar{3}4$, having approximately the same spacing, are produced by X-rays of the same length. Of these 2 spots $05\bar{1}$ is much more intense. Consequently planes for which $(h + k + l) = 4$ give larger effects than planes having $(h + k + l) = 2$. A consideration of spots due to $\bar{2}33$ and $2\bar{3}3$ and of spots due to $6\bar{3}1$ and $\bar{4}15$ leads to the same conclusion. This means that α/a must have a value about 0.3 rather than near to 0.4.

It is difficult to find points having approximately the same values for the spacing and different values of $(h + k + l)$ produced by X-rays of the same wave length. In order to place the chlorine atoms more accurately it is necessary to make use of the assumption, generally assumed to be correct, that the amplitude of the reflected X-ray wave is inversely

proportional to the spacing of the reflecting plane. Accepting this assumption a reduction of the form

$$\text{spacing} \propto (\text{Cs} \approx \text{I} + 2\text{Cl} \cos 2\pi n\alpha/a(h + k + l))$$

can be used in comparing the amplitudes of the beams reflected from planes of different spacings

Results from the first unsymmetrical photograph show that the intensity of reflection of X rays of the same wave length by different planes is as follows:

hkl	Intensity	Relative spacing	Amplitude
$1\bar{3}\bar{2}$	3 2	$0.262 \propto (260 + 71\epsilon) = 68.1 + 18.2\epsilon$	
$0\bar{5}\bar{1}$	3 0	$0.198 \propto (260 + 71\epsilon') = 51.5 + 11.8\epsilon'$	
141	2 0	$0.229 \propto (260 + 71\epsilon) = 59.5 + 16.1\epsilon$	
$1\bar{5}\bar{2}$	2 0	$0.183 \propto (260 + 71\epsilon) = 47.6 + 12.6\epsilon'$	
$3\bar{2}\bar{3}$	0 5	$0.206 \propto (260 + 71\epsilon) = 53.6 + 14.4\epsilon$	

$$\epsilon = \cos 2\pi\alpha/a \times 2$$

$$\epsilon' = \cos 2\pi\alpha'/a \times 2$$

Results from the second unsymmetrical photograph confirm those from the first. If the relative amplitudes of the X-rays are determined by substituting various values for α/a around 0.3 (the approximately determined position of chlorine) it is found that the observed intensity relations can be obtained only when α/a has a value from about 0.312 to about 0.317.

The following points are due to X-rays of the same wave length. The order of intensity is the order of writing

hkl	Relative spacing	$h+k+l$
015	0.198	4
$1\bar{2}\bar{5}$	0.183	4
$2\bar{3}\bar{3}$	0.206	2
116	0.171	6
$\bar{1}38$	0.129	10
$\bar{1}27$	0.148	8
$3\bar{4}\bar{5}$	0.139	4
$0\bar{3}\bar{7}$	0.128	4
019	0.120	10
$4\bar{5}\bar{5}$	0.124	6

The very favorable conditions for planes having $(h + k + l) = 10$ indicate that the chlorine atoms must lie near to 0.312 rather than to 0.317.

It is thus seen that the chlorine atoms must lie close to 0.31 of the length of the diagonal of the unit rhombohedron on either side of the cesium atom. This, of course, is on the assumption that the chlorine atoms lie nearer to the iodine atom. Since cesium and iodine have atomic weights so nearly equal (133 and 127), they must reflect X-rays to nearly the same extent if the generally accepted law of proportionality between reflecting power and atomic number is true. It then will be a very diffi-

cult matter to determine whether the chlorine atoms really lie nearer to the cesium or to the iodine atom.

When the arrangement of atoms in the unit of structure of cesium dichloro-iodide which we have obtained above is used for calculating the amplitudes of the X-rays reflected by various planes, there is a qualitative agreement with the observed intensities of the spots. Certain difficulties are met, however, if it is attempted to make this agreement quantitative. These attempts require the use of those assumptions, generally supposed true, which give the relation between intensity of reflection and spacing of like planes¹ and intensity of reflection and mass of the atom.²

The qualitative agreement is, however, so uniformly good that there can be little doubt as to the truth of the determination given here. The fact that this agreement is not quantitative points to the necessity, so many times urged before, for a careful and accurate investigation of the fundamental relations connecting reflection and spacing and reflection and weight of the reflecting atom.

This structure for cesium dichloro-iodide may be considered as closely analogous to that of sodium chloride and the other alkali halides. From this point of view the group (ICl_2) may be thought of as replacing the halogen of the simple compound. As a result of this substitution the unit cube is deformed into a rhombohedron by extension along the body diagonal.

The author wishes to express his thanks to Professor L. M. Dennis, who suggested this investigation, and to the Department of Physics for the use of the necessary apparatus. Most especially he is under great obligation to Dr. S. Nishikawa, whose untiring advice and aid has made this determination possible.

Summary.

The crystal structure of cesium dichloro-iodide (rhombohedral) has been determined. The body-centered unit rhombohedron contains one molecule. The cesium atom is placed either at the center or the corner of this unit and the iodine atom either at the corner or the center. Two chlorine atoms lie on the long diagonal of the rhombohedron very close to 0.31 of its length from the corners. Because of the *supposedly* very nearly equal scattering powers of cesium and iodine, it is impossible at present to decide which of these 2 possibilities is correct.

ITHACA, N. Y.

¹ W. H. Bragg and W. L. Bragg, *loc. cit.*, Chap. XI.

² W. H. Bragg and W. L. Bragg, *ibid.*, Chap. VIII.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No 125.]

THE FREE ENERGY OF DILUTION AND THE TRANSFERENCE NUMBERS OF LITHIUM CHLORIDE SOLUTIONS.

BY DUNCAN A. MACINNES AND JAMES A. BEATTIE

Received March 12, 1920.

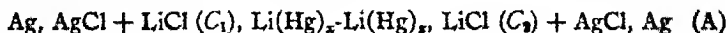
1. Purpose and Outline of Investigation.

The following investigation, which includes measurements of the electromotive forces of cells containing solutions of lithium chloride follows, in general outline, the research by MacInnes and Parker¹ on solutions of potassium chloride. Both investigations involve measurements on cells with and without liquid junctions, from which it will be recalled that the activities of the ions and the transference numbers of the salt may be computed.

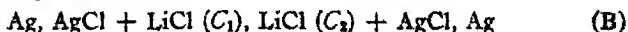
Lithium chloride was chosen for this research since lithium is the lightest of the alkali metals, and its salts probably indicate one extreme of behavior in their physical properties. Further, the transference numbers of lithium chloride change rapidly with the concentration, a phenomenon which, it seemed to us, needed further investigation, since it has an important bearing on the theory of strong electrolytes.

As the properties of lithium chloride and of metallic lithium differ greatly from those of potassium chloride and metallic potassium, quite different procedures from those adopted by MacInnes and Parker were necessary in certain parts of the work. Improvements in manipulation have also been developed during the course of both investigations. For these reasons the procedure finally adopted will be described below in some detail. Pearce and Mortimer² have carried out a research on lithium chloride solutions similar to the one to be described. Their results, however, lead to very different conclusions from those arrived at in this investigation. Further reference will be made to their work in a later section.

Our investigation included measurements, at 25°, of cells, without liquid junction of the form



and cells with liquid junction



in which the concentrations, C_1 and C_2 , varied between 3.0 and 0.001 molal.

The work has been carried out with the aid of a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our gratitude.

¹ THIS JOURNAL, 37, 1445 (1915).

² *Ibid.*, 40, 509 (1918).

In the earlier paper¹ it was shown that the electromotive force of a concentration cell without liquid junction, E , can be expressed by the relation:

$$E = \frac{RT}{F} \ln \frac{a_1^+ a_1^-}{a_2^+ a_2^-} \quad (1)$$

in which $a^+ a^- a_2^+ a_2^-$ are the "activities"² of the positive and negative ions, respectively, at 2 salt concentrations. It was further shown that if the transference number, n , is a constant within the concentration range involved, the electromotive force of a cell with liquid junction, E_l , can be expressed by the equation:

$$E_l = \frac{nRT}{F} \ln \frac{a_1^+ a_1^-}{a_2^+ a_2^-} \quad (2)$$

n , being the transference number of the ion to which the electrodes of the cell are not reversible

If, however, the transference number changes with the concentration, as is the case with nearly all electrolytes, E_l will be an integral, between limits, of the equation

$$dE_l = \frac{RT}{F} n d \ln (a^+ a^-). \quad (3)$$

Since n , a^+ and a^- are functions of the concentration of the electrolyte, Equation 3 is a complete differential. This expression will be referred to again in a later section

2. The Concentration Cells without Liquid Junctions.

The concentration cells without liquid junctions involve (a) silver-silver chloride electrodes, (b) lithium amalgam electrodes, (c) air-free lithium chloride solutions.

(a) **Silver-silver Chloride Electrodes.** - The supports for the silver-silver chloride electrodes consisted, as in the work of MacInnes and Parker, of pieces of fine platinum gauze (about $1\frac{1}{2}$ cm. sq) welded to platinum wire which, in turn, made contact with mercury through glass tubes. The gauze was given a thick coating of silver from a solution of potassium silver cyanide, using 3 milliamperes, per electrode, for 24 hours. After thorough washing, a coating of chloride was formed on the silver by electrolyzing in a lithium chloride solution with a current of 5 to 7 milliamperes per electrode for 20 minutes. A variation from the former procedure was the formation of this chloride in lithium chloride solutions of the same concentration as those in which the electrodes were to be used. This avoided possible inclusions in the chloride of small amounts of electrolyte of unknown concentration, and resulted in much more

¹ MacInnes and Parker, *loc cit*

² Lewis, *Proc. Am. Acad.*, 43, 259 (1907) A discussion of the concept of "activity" is also given in a recent paper by Noyes and MacInnes, *This Journal*, 42, 239 (1920).

constant and reproducible electrodes. We feel that our success with these electrodes is, to a large extent, due to this method of preparation. The electrodes for 0.001 and 0.003 *N* solutions were, however, formed in 0.01 *N* lithium chloride, since, at these low concentrations, it was difficult to get enough current through the solutions and the electrolysis produced silver chloride in a non-adherent form.¹ A small rubber stopper on each glass stem, as is shown in Fig. 3, aided greatly in the handling of these electrodes, as they frequently became damaged while being pushed through the holes in the large rubber stoppers used in the earlier work. The electrodes used were usually within 0.03 mv. of the same potential. In the more dilute solutions, however, the differences occasionally reaches 0.05 mv. When two electrodes, formed in different solutions, were put into the same solution they rapidly assumed the same potential within 0.1 or 0.2 mv., indicating that the same modification of silver chloride was present on all the electrodes.

(b) **Lithium Amalgam Electrodes.**—The lithium amalgam electrodes (H in Fig. 2) differ from those used by MacInnes and Parker in having the amalgam flow in a thin stream from fine capillaries instead of overflowing as large drops from a cup-shaped tip. In this investigation, constant potentials were not obtained with the latter design. The lithium amalgam apparently reacts more rapidly with water than potassium amalgam does under the same conditions, as is, possibly, to be expected from the higher potential of the former metal.

In the preparation of lithium amalgam, a number of attempts were made to remove the surface layer of oxide from the lithium by running the molten metal through glass capillary tubing. The glass walls of the tubing were, however, rapidly disintegrated by the metal. The amalgam was, therefore, made in the vessel A as represented in Fig. 1. Pellets of metallic lithium were inserted through tube B, which was then connected to a mercury still. After distilling the desired amount of mercury, the tube was sealed off. Since a coating of oxide covered the lithium, solution did not take place until the mercury was heated. After complete amalgamation the apparatus was inverted as shown and allowed to stand for a week to permit the lithium oxide to separate and rise to the top. The amalgam could then be drawn out through the capillary tube and stopcock C and D. The amalgam was then transferred to another flask, of similar construction, which further separated the oxide. The amalgam electrode vessel was filled by connecting the 2 vessels by means of a T-tube, one arm of which was joined to a vacuum pump.



Fig. 1.

¹ An interesting explanation of the phenomenon is given by Reedy, *Am. J. Sci.*, 40, 281 (1915).

(c) **Air-free Lithium Chloride Solutions.**—The work on potassium chloride solutions showed definitely that air must be *completely* excluded from the solutions that come in contact with the amalgam electrodes since oxygen reacts instantly with the amalgam, reducing its alkali metal content and increasing the ion concentration of the surrounding electrolyte, both of which have the same result, *i. e.*, to reduce the potential at the electrode. Since solid lithium chloride is very hygroscopic, the solutions could not be made up by adding weighed amounts of the salt to water, in an inert atmosphere, as in the work with potassium chloride. The procedure with lithium chloride adopted was to make up a strong solution of the salt and determine its concentration, by weight, by precipitating the chloride with silver nitrate. A round-bottomed flask (F of Fig. 2) was weighed with its stopper and connecting tubes, a quantity of the strong solution added, and the flask weighed again. The solution was then vigorously boiled for some time under reduced pressure to remove the dissolved air. In the meantime, water was collected hot with a rapid evolution of steam in a resistance glass container, from the still for conductivity water, and boiled in a partial vacuum. The free space in the container was then filled with nitrogen. Using a pressure of this gas the air-free water was run through glass tubing into the round-bottomed flask F, until nearly the right dilution was attained, special provision being made to keep air out of all connections. The flask F, was again weighed, and water added in successive small amounts, out of contact of air, until the required concentration (within 0.3%) was obtained. Our belief that air was completely excluded from the solutions is borne out by the reproducibility of the measurements of the cells without liquid junctions.

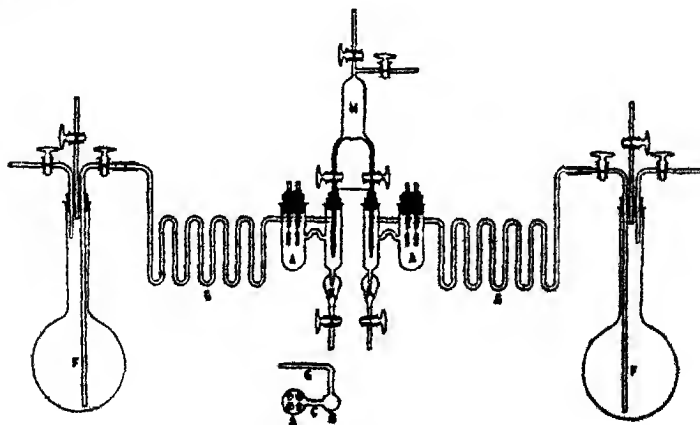


Fig. 2.

The complete cell without liquid junction is shown in Fig. 2, which is nearly self explanatory. The grids of glass tubing G, served to bring the flowing solutions to the exact temperature of the thermostat, and gave a useful flexibility in making connections with the flasks F. The rejected solutions and amalgam flowed through the air spaces K into tubes leading through the bottom of the thermostat. The silver-silver chloride electrodes were placed in the vessels A separated by a bent tube from the flowing solution.

3. The Concentration Cells with Liquid Junction.—Our greatest improvement in manipulation, since the work with KCl solutions, was, possibly, made in the concentration cells with liquid junctions. A complete cell is shown in section of Fig. 3. In filling the cell the more concentrated solution was placed in Vessel A, the Ag-AgCl electrodes were placed in the side tubes, and additional solution was run into Tube E until D was completely filled, when the pinchcock F was closed.

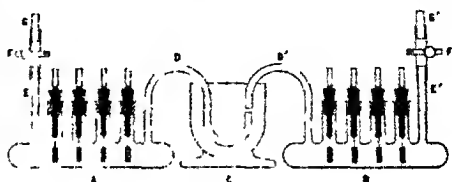


Fig 3.

The vessel B was then filled, with the dilute solution, to the end of the tube D'. The D and D' were then placed, as shown, into the empty cup C. The whole apparatus was next immersed in a thermostat and the electrodes were allowed to come to equilibrium, when a solution of a strength intermediate between those in the vessels A and B was cautiously run into cup C. Readings of the electromotive force of the cell were then made. The potentials of liquid junctions formed in the manner described were surprisingly constant, often showing no perceptible change in several hours and seldom decreasing more than 0.1 mv. in 24 hours. The potential is independent of the concentration of the intermediate solution provided it is within the concentration limits of the solutions in A and B; this was shown in an extended investigation on potassium chloride concentration cells by F. F. Footitt and one of the present authors. Reversal of the positions of the solutions in the cell (i. e., the dilute solution in vessel A) leads to low and erratic results.

The one condition necessary for the formation of a reproducible liquid junction between 2 differently concentrated solutions of the same electrolyte is the maintenance of the concentration gradient at all points between the stronger and dilute solutions at values which are either negative or zero; that is, the concentration must either be constant or steadily decrease. If this condition is fulfilled, the potential is independent of the distance through which the mixing of the 2 solutions takes place. In addition it is, of course, necessary that the solutions around the electrodes

remain constant in composition, a condition which is difficult to attain unless mixing of the solutions due to volume changes of gas in the vessels, differences of specific gravity of the solutions, etc., is carefully guarded against. Reproducible junctions involving 2 different electrolytes cannot, however, be made in the manner just described.

All the measurements were made in a thermostat kept at $25^{\circ} \pm 0.02^{\circ}$. The potentials were determined with a Leeds and Northrup potentiometer which was carefully calibrated during the investigation. The standard cell was compared, several times during the investigation, with 2 cells which had been recently calibrated by the Bureau of Standards. The thermometer used was compared with a thermometer calibrated by the same bureau.

4. Materials and Methods of Purification.

Lithium Chloride.—Pure lithium carbonate was treated with pure hydrochloric acid and the resulting chloride was crystallized 5 times from conductivity water. An attempt was made to crystallize the salt from pyridine, but it was found difficult to remove the last traces of the solvent without charring and making the salt alkaline.

Lithium.—The pure metallic lithium used in making the amalgams was very kindly supplied by Dr. A. W. Hull, of the General Electric Co.

Mercury.—The mercury was covered with dil. nitric acid and agitated by a current of air for a week. It was then passed in a thin stream through a tube, about 2 meters long, filled with dil. nitric acid, after which it was distilled several times under reduced pressure.

Water.—Conductivity water was prepared in the special still in this laboratory.

5. The Results of the Electromotive Force Measurements.

The potentials of the cells without liquid junction, of the form: $\text{Ag} + \text{AgCl}$, LiCl (c_1), Li(Hg)_x , LiCl (c_2), $\text{Ag} + \text{AgCl}$, are given in Table I. Each figure for the electromotive force of a cell refers to a complete assembling of the cell, involving *freshly prepared solutions*, and, in each duplicate determination, a different concentration of amalgam.

The potentials of the cells with liquid junction are given in Table II. For each determination recorded the electrodes were reformed, i. e., plated with silver and coated with silver chloride. As shown in Fig. 2, there were 4 electrodes in each solution. The potential given is the average of readings of every possible combination of one electrode in each half cell, or 16 readings in all. The third column of the table gives the average deviation of these readings. Since these results demonstrated the reproducibility of the electrodes, only one electrode in each solution was used in the cells without liquid junction.

TABLE I.
 Electromotive Forces of Cells without Liquid Junction.

Conc. LiCl Solns Mols per 1000 g. water.		Conc of Lithium Amalgam (Approx). %	E m. f. Millivolts
C ₁ .	C ₂ .		
3.0	0.3	0.001	141.71
		0.005	141.69
1.0	0.1	0.015	116.52
		0.005	116.48
0.3	0.1	0.001	53.73
		0.005	53.67
0.3	0.03	0.005	111.18
		0.002	111.16
0.1	0.01	0.01	110.57
		0.002	110.55
		0.005	110.53
0.03	0.003	0.005	112.80
		0.015	112.70
0.01	0.001	0.001	114.0
		0.001	113.8

 TABLE II.
 Electromotive Forces of Cells with Liquid Junctions.

Conc. LiCl Solns Mols per 1000 g. Water.		E m f of cells Millivolts.	Average deviation
C ₁ .	C ₂ .		
3.0	0.3	39.574	±0.007
		39.577	0.012
1.0	0.1	35.435	0.025
		35.421	0.019
0.3	0.1	16.401	0.021
		16.420	0.016
		16.420*	
0.3	0.03	35.210	0.020
		35.211	0.014
0.1	0.01	35.885	0.015
		35.893	0.021
0.03	0.003	37.595	0.019
		37.615	0.021
0.01	0.001	39.074	0.012
		39.039	0.021

* Determined with a "flowing" junction by Mr. Y. L. Yeh of this laboratory.

6. Discussion of Results.

(a) Activities and Activity Coefficients.—Equation 1 can be put in the form

$$E = \frac{2RT}{F} \ln \frac{a_1}{a_2}$$

in which a_1 and a_2 are the (geometrical) mean values of the activities of the two ions at the concentrations C_1 and C_2 . From this equation the activity ratios for any pair of concentration ratios can be obtained. To obtain the activities at the various concentrations at which measurements were made, the activity was assumed to be equal to the concentration multiplied by the conductivity ratio Λ/Λ_0 at the lowest concentration (0.001 N). A plot of the potentials of the cell without liquid junction showed, however, that the value assigned in Table I to the cell containing 0.01 and 0.001 N solutions is about 0.5 millivolt too low, a result which would occur from a trace of oxygen in solution, or a very slight reaction of the amalgam with water. To either of these the potentials at the amalgam electrode in the 0.001 N solution would be very sensitive. From the plot just mentioned a potential of 114.43 mv. was interpolated for the 0.01–0.001 N cell. By the obvious methods of computation the activity values in Col. 2 of Table III were obtained. The activity coefficients in Col. 3 are, of course, the activities divided by the corresponding concentrations. The table also includes in Col. 4 the "degrees of dissociation," Λ/Λ_0 computed from the conductance data of Kohlraush and Maltby.¹ As pointed out in a recent paper,² no relation between activity coefficients and "degrees of dissociation" has so far been discovered, the former, in the cases of lithium chloride, hydrochloric acid and potassium hydroxide solutions, being at low concentrations smaller, and at high concentrations larger, than the latter. Multiplication of the "degrees of dissociation" by the viscosity ratio (*i. e.*, the viscosity of the solution divided by the viscosity of water) increases the difference between the activity coefficient and the "degree of dissociation" up to about 0.5 N . Above this point the viscosity correction is in a direction that decreases the discrepancy between the 2 series of numbers, but is entirely inadequate.

TABLE III.

Concentrations of LiCl.	Activity.	Activity coefficient	Conductance ratio= "degree of dissociation"
0.001	0.000976	(0.976)	(0.976)
0.003	0.00283	0.945	0.962
0.01	0.00905	0.905	0.932
0.03	0.0254	0.848	0.899
0.1	0.0779	0.779	0.834
0.3	0.221	0.738	0.759
1.0	0.752	0.752	0.641
3.0	3.491	1.164	0.458

¹ "Leitvermögen der Electrolyte."² Noyes and MacInnes, *THIS JOURNAL*, 42, 239 (1920).

(b) **The Transference Numbers.**—If the potential of a cell with liquid junction is divided by that of a cell without liquid junction, both cells containing the same pair of solutions, of concentrations C_1 and C_2 , the transference number (of the ion to which the electrodes of the cell with liquid junction is not reversible) is obtained, provided that the number is a constant within the given concentration limits. This is evident from Equations 1 and 2. If, however, the transference number is a variable, the division indicated above gives a figure whose value lies between the transference numbers at C_1 and C_2 . A method by which the transference numbers may be obtained, at any concentration within the concentration limits studied, is outlined below.

According to Equation 3 the electromotive force of a cell with liquid junction is an integral of

$$dE_t = 2N \frac{RT}{F} d \ln a \quad (3a)$$

in which a is the geometrical mean of the activities of the ions. The corresponding equation for the cell without liquid junction is:

$$dE = 2 \frac{RT}{F} d \ln a$$

Now, if the electromotive forces of cells of the latter type are plotted as ordinates and the logarithms of the corresponding mean activities as abscissas, a straight line, with a slope equal to $2RT/F$ is necessarily obtained (line A in Fig. 4). The corresponding line for the cells with liquid junction is the curve B. In plotting this curve, the electromotive force for a cell containing lithium chloride at concentrations 0.01 and 0.1 is added to the potential for concentrations 0.001 and 0.01 N , etc. The ordinates for 0.03 and 0.003 N are obtained by subtracting the appropriate potentials from Table II from the ordinate for 0.3 N . It is interesting to note that the result is a smooth curve, even on a large scale plot. The slope of this curve, as can be

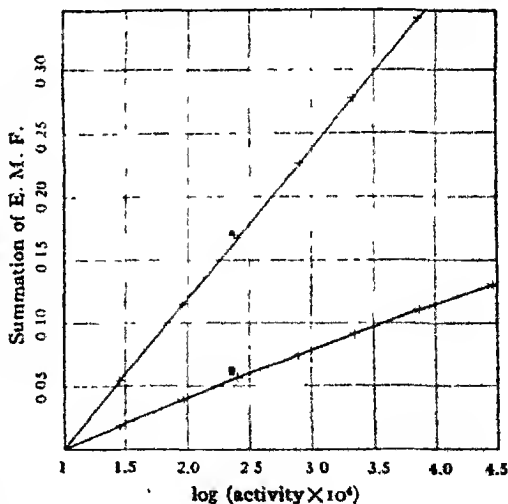


Fig. 4.

be

from Equation 3, is nRT/F , and the transference number at any activity, and thus at any concentration, is the ratio of the slopes of the lines A and B at the corresponding points. To obtain the slope of line B the following empirical equation,

$$E_1 = -43.865 + 45.363 (\log A) - 1.4902 (\log A)^2, \quad (5)$$

in which E is the summed up electromotive force and A the activity ($\times 10^4$), was computed by means of the method of least squares. This expression was then differentiated with respect to $\log A$ and its constants divided through by the (constant) slope of line A [0.011830], with the following result:

$$n = 0.3834 - 0.02529 \log A \quad (6)$$

In Fig. 5 transference numbers computed from Equation 6 are plotted as ordinates and logarithms of the corresponding concentrations as abscissas. Jahn and Goldhaber's¹ values at 18°, Washburn's² determination at 25°, and two measurements by Bein³ at 22.5° and 25°, are also included.

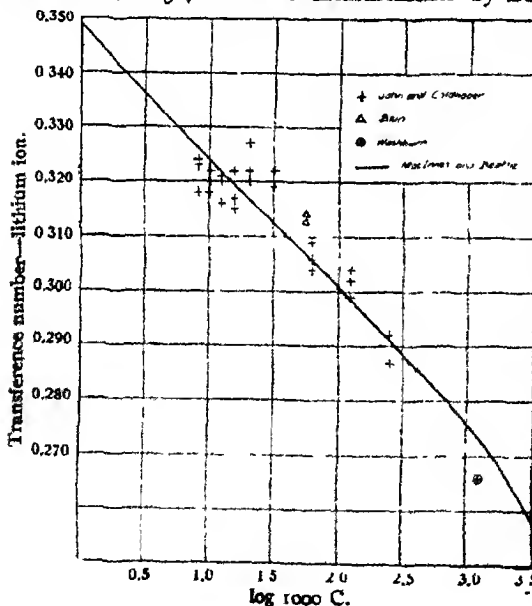


Fig. 5

The fact that this treatment of the results yields transference numbers at definite concentrations removes one objection to the method which is, in our opinion, the most accurate method of obtaining these important constants in the cases where its application is possi-

¹ *Z. physik. Chem.*, 37, 673 (1901).

² *Technology Quarterly*, 21, 288 (1908); the solution contained 0.1 mol raffinose.

³ *Z. physik. Chem.*, 27, 1 (1898).

ble. Transference numbers at round concentrations are given in Table IV and compared with the "best values" as given in Noyes and Falk's compilation¹ of all of the more recently determined data.

TABLE IV.
Transference Numbers of Lithium Ion in Lithium Chloride.

Conc.	E. m. f. method	"Best value" Hittorf method
0.001	0.359	..
0.005	0.341	
0.01	0.334	0.332
0.02	0.327	0.328
0.05	0.318	0.320
0.10	0.311	0.313
0.20	0.304	0.304
0.30	0.299	0.299
0.50	0.293	
1.0	0.286	
2.0	0.276	
3.0	0.268	

7. Discussion of Previous Work.

As has been stated, Pearce and Mortimer² have carried out an investigation covering much the same field as the research described in this paper, including measurement with cells containing several other solvents than water. Their results and conclusions, however, differ widely from ours. For instance, the value they record for the 1.0 — 0.1 *N* concentration cell without liquid junction is 2 mv. lower than that given in Table I. This difference increases progressively with dilution until it reaches about 12 mv. for the 0.05 — 0.005 *N* cell. Though the authors state that "greatest care was taken to secure the least possible contact with air," it is evident that oxygen was not sufficiently excluded from their solutions. As would be expected, the effect of this dissolved oxygen on the potential increases with decreasing concentration. The work on potassium chloride cells³ showed that constant, though erroneous, potentials can be obtained from oxygen bearing solutions. Their values also indicate a decrease of activity coefficients with increasing dilution (below 0.1 *N*). This is shown by no other electrolyte, and freezing-point measurements give evidence, independent of that outlined in this article, that it is not the case for lithium chloride solutions. The potentials of their cells with liquid junction, being uninfluenced by the presence of oxygen, show somewhat closer concordance with the figures given in Table II.

The transference numbers computed from Pearce and Mortimer's

¹ THIS JOURNAL, 33, 1436 (1911).

² *Ibid.*, 40, 509 (1918).

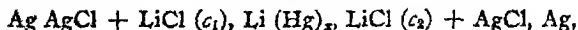
³ MacInnes and Parker, *loc. cit.*

data agree roughly with the early data of Kuschel,¹ as quoted in a compilation by Kohlrausch and Holborn.² Their results, however, vary widely from the later and far more accurate transference measurements by Jahn, Bein and Washburn.³

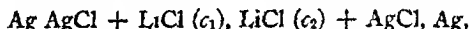
Recently, Allmand and Polack⁴ have published the results of measurements on cells of the type: $\text{Hg}, \text{HgCl} + \text{NaCl}, \text{Na}(\text{Hg})_x$. Their work can only be regarded as preliminary, especially for the more dilute solutions, since no attempt was made to keep oxygen out of their solutions.

8. Summary.

The electromotive forces of cells without liquid junction



in which the concentrations C_1 and C_2 varied between 3.0 and 0.001 N have been measured at 25° , and the activities of the ions of the salt have been computed. With the aid of measurements on cells with liquid junction



the transference numbers of the ions have been obtained. Since these numbers, for lithium chloride, change rapidly with the concentration, a method has been devised by which the numbers can be computed from the electromotive force measurements and expressed as a function of the ion activity. The value of the transference number at any given concentration, within the range studied, can thus be obtained.

CAMBRIDGE, MASS.

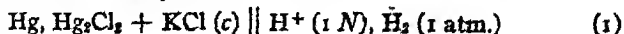
[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO 126]

THE ACTIVITY COEFFICIENT OF NORMAL POTASSIUM CHLORIDE SOLUTION AND THE POTENTIAL OF THE NORMAL CALOMEL ELECTRODE.

BY JAMES A. BEATTIE.

Received March 12, 1920

Since the normal hydrogen electrode and the normal calomel electrode are both used as standards in electromotive force calculations, it is desirable to know accurately the potential difference between them. The electromotive force of the system



is given by the equation

¹ *Wied. Ann.*, 13, 289 (1881). Kuschel used diaphragms of gold beaters skin so his results were probably seriously influenced by electroendosmosis.

² "Leitvermögen der Electrolyte." The determinations were not made by Kohlrausch and Holborn, as stated by Phelps and Mortimer.

³ *Loc. cit.*, see p. 1126.

⁴ *J. Chem. Soc.*, 115, 1020 (1919).

$$E = \bar{E} + \frac{RT}{F} \log c\alpha \quad (2)$$

where \bar{E} is the specific electrode potential of the calomel electrode, i. e., its potential when the activity of the chloride ion is unity, and $c\alpha$ is the activity of that ion in a c normal solution. It will be noted that the potential of the hydrogen electrode is assumed to be zero. If the activity of the chloride ion in a one normal potassium chloride solution is used in Equation 2, the value of E calculated is the potential of the normal calomel electrode in terms of the normal hydrogen electrode.

From their own measurements Noyes and Ellis¹ calculate \bar{E} , the specific electrode potential of the calomel electrode, to be -0.2700 volt at 25° . Using a value of the chloride ion activity in N potassium chloride extrapolated from MacInnes and Parker's² results (which extend only to 0.5 molal), they find -0.2824 volt as the value for the potential difference between the normal calomel and normal hydrogen electrodes. Lewis, Brighton and Sebastian,³ by a different method, arrive at -0.2828 volt for this potential, but their "normal electrode" includes the liquid junction potential between 0.1 and $1.0 N$ potassium chloride solutions. The effect of this junction will be considered later.

Since the apparatus measuring the potentials of concentration cells without liquid junction, described in the article immediately preceding this, was in operation, I undertook, at the suggestion of Dr. A. A. Noyes, the direct determination of the activity ratio between 1.0 and 0.1 molal⁴ potassium chloride solutions, to provide the necessary data for the calculation of the ion activity of a N potassium chloride solution.

The procedure was the same as that in the preceding article except that the solutions and amalgam were made up by the methods described by MacInnes and Parker.

TABLE I

The E M F of KCl Concentration Cells, without Transference, at 25° .
 $\text{Ag, AgCl} + \text{KCl, K(Hg)}_s - \text{K(Hg)}_s \text{KCl} + \text{AgCl, Ag}$

			E M F
1 0 m	0 004	0 1 m	-0 10650
1 0 m	0 004	0 1 m	-0 10660

Using the equation $\bar{E} = \frac{2RT}{F} \log \frac{c_1\alpha_1}{c_2\alpha_2}$ and substituting -0.10655 for E gives 0.7956 for the activity ratio of 1.0 to 0.1 molal potassium chloride. This value, together with those of MacInnes and Parker, and Harned⁵

¹ THIS JOURNAL, 39, 2532 (1917).

² *Ibid.*, 37, 1445 (1915).

³ *Ibid.*, 39, 2258 (1917).

⁴ In this article "normal" will be used to denote a solution containing one equivalent of solute in 1000 cc. of solution at the temperature under consideration, and "molal" to denote a solution consisting of one mol of solute in 1000 grams of water.

⁵ THIS JOURNAL, 38, 1986 (1916).

were used to obtain the table of activities for potassium chloride given in an article by Noyes and MacInnes.¹ It must be remembered that it is the activity of the *chloride ion* that must be used in Equation 2. However, I will assume, following MacInnes,² that the activities of the 2 ions of potassium chloride are the same.

From the density of a 1 *N* potassium chloride solution, which is given as 1.0428 in "Landolt-Börnstein Tabellen," its *molal* concentration is found to be 1.0328, and the corresponding activity obtained from a plot of the values given by Noyes and MacInnes (against logarithms of concentration) is 0.592.

The potential of the normal calomel electrode then becomes, by Equation 2,

$$E = -0.2700 + 0.5915 \log 0.592 \times 1.0328,$$

or -0.2826 volt. This, of course, assumes the correctness of Noyes and Ellis' value for the specific electrode potential.

The calculation of the liquid junction potential of 0.1 to 1.0 *N* potassium chloride can be made by the formula of MacInnes,³ $E_l = E_i (1 - 1/2n)$, where E_l is the liquid junction potential, E_i the electromotive force of the corresponding concentration cell with transference and n the cation transference number. Lewis and Sebastian,⁴ and Harned⁵ have both measured E_i for 0.1 to 1.0 *N* potassium chloride solutions; the former give 0.5290, and the latter 0.5287. Using the value 0.5290 and the transference number 0.496, from Table II below, the liquid junction potential is found to be +0.0004 volt which added to Lewis, Sebastian and Brighton's value (-0.2828) gives -0.2824 for the potential difference between the normal hydrogen and normal calomel electrodes.

The transference number of the potassium ion in a 1.0 to 0.1 molal potassium chloride solution is the ratio of the e. m. f. of the cell with liquid junction (-0.5290) to that without liquid junction (-0.10655) which equals 0.496. It can be shown that this is the transference number in a 0.3162 molal solution, *i. e.*, the geometrical mean of 1.0 and 0.1. Table II gives a résumé of the transference numbers of the potassium ion in potassium chloride solutions obtained from this work and that of MacInnes and Parker.

Since the transference number is practically constant over the entire range of concentration, it is not necessary to use the method of computation given in the previous article.

¹ THIS JOURNAL, 42, 239 (1920).

² *Ibid.*, 41, 1086 (1919).

³ *Ibid.*, 37, 2301 (1915).

⁴ *Ibid.*, 39, 2245 (1917).

⁵ *Loc. cit.*

TABLE II.

The Transference Number of Potassium Ion in Potassium Chloride Solutions at 25°.

Concentration range.	Mean concentration.	Transference number
1.0-0.1	0.3162	0.496
0.5-0.05	0.1581	0.498
0.1-0.01	0.03162	0.496
0.05-0.005	0.01581	0.494

Summary.

The work of MacInnes and Parker on the activity values and transference numbers of potassium chloride solutions is extended to one molal concentration.

The potential of the normal calomel electrode is calculated to be -0.2826 volt, agreeing quite well with Lewis, Sebastian and Brighton's value (-0.2824 volt), when corrected for the liquid junction potential between 0.1 and 1.0 *N* potassium chloride solutions.

CAMBRIDGE, MASS

[CONTRIBUTION FROM THE FLIXED NITROGEN RESEARCH LABORATORY]

PRESSURE MEASUREMENTS OF CORROSIVE GASES. THE VAPOR PRESSURE OF NITROGEN PENTOXIDE.¹

BY FARRINGTON DANIELS AND ARTHUR C. BRIGHT

Received March 20, 1920.

Pressure measurements of the higher oxides of nitrogen and nitric acid are difficult because these substances attack materials on which the chemist usually relies, including rubber tubing, mercury and stopcock grease. Since such measurements are necessary for the proper study of nitrogen fixation processes, an apparatus made entirely of glass has been devised which is capable of measuring gas pressures conveniently and accurately over a wide range of conditions. With it the vapor pressure of nitrogen pentoxide has been determined. Further related researches are also in progress.

Description of the Apparatus.

The vapor pressure apparatus in its final form is shown in Fig. 1. Its unique feature consists of the glass diaphragm, movement of which makes or breaks an electrical circuit and permits balancing of an air pressure against the unknown pressure. The air pressure is read directly on a mercury manometer as shown.

The method of making the glass diaphragm is shown in Fig. 2. A small bulb of glass, with a thin end, is blown as shown in the first illustration. This is flattened by plunging the end into a flame, momentarily, while rotating. A little practice is necessary to judge properly the ex-

¹ Published by permission of Mr. George J. Roberts, special Assistant to the Chief of Ordnance, U. S. A. and Dr. Mellow Whitney, Chief, Bureau of Soils.

tent of the flattening process and to give sufficient annealing without destroying the shape. Previous to flattening, the whole bulb and a short length of the stem are carefully platinized with several applications of a

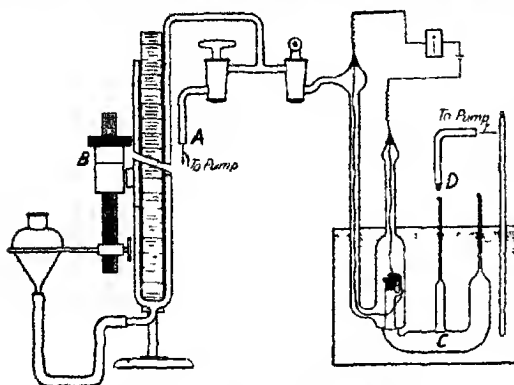


Fig. 1.—Vapor pressure apparatus.

very thin platinizing solution and heated to dull redness after each application. A glass arm, with rounded end platinized, is fused on as shown in the third illustration, and adjusted so that after cooling it presses gently against the center of the diaphragm. After twisting platinum wires tightly around the base of the bulb and around

the platinized arm, the whole is mounted in a glass shell and fused to the vessel which is to contain the material to be tested. The assembled apparatus is shown at C in Fig. 1.

The dimensions of the glass diaphragms varied somewhat but averaged about one cm. in diameter and between 0.1 and 0.2 mm. in thickness. All those which did not make and break electrical contact with a pressure difference of a millimeter of mercury or less were rejected. The most sensitive ones likewise were not used in the present research because the chance of breakage was too great. No difficulty was encountered from this source if the inner compartment was never evacuated without first evacuating the outer one. All the diaphragms used withstood a pressure of more than an atmosphere outward and most of them were capable of withstanding one atmosphere inward. They gave the same zero

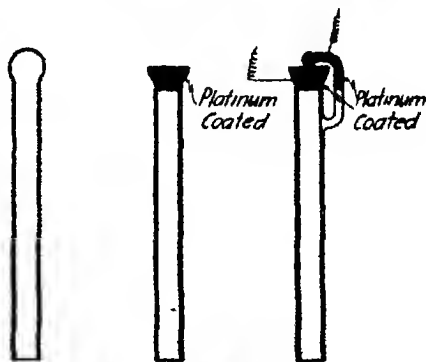


Fig. 2.—Glass diaphragm.

reading at all temperatures over a range of 75° , even after withstanding pressure differences of an atmosphere. The diaphragms actually used were sensitive to a fraction of a millimeter and accurate to a millimeter.

The electrical circuit comprised a small portable galvanometer and a

low voltage cell (silver and platinum in an electrolyte) which gave proper deflections, or a dry cell with a high resistance in series. It was essential to have the voltage so low that there was no sparking between the platinized surfaces. Electrical connection was made through the glass shell by short pieces of platinum wire, welded to copper wires. It was necessary to prepare the platinized surfaces with great care and to keep them scrupulously clean.

Several all-glass manometers are described in the literature,¹ most of which depend on the movement of glass indicators or spirals. It is thought that the one described here is to be preferred because of its simplicity and its freedom from optical systems. This apparatus may be used in high pressure bombs or in high temperature furnaces (if made of quartz) where the visual observation required by all other types is more difficult.

Preparation of Nitrogen Pentoxide.

The nitrogen pentoxide was prepared by dehydration of nitric acid with phosphorus pentoxide by the Berthelot-Weber² method and purified by sublimation in ozone as recommended by Russ and Pokorny.³ Conc. nitric acid was distilled from an excess of sulfuric acid. About 25 cc. of this 100% acid was placed in a glass-stoppered washing bottle with the inlet sealed off, and mixed with small portions of phosphorus pentoxide until a thick paste resulted. This operation was carried out carefully with cooling, in ice and salt, to prevent decomposition of the nitrogen pentoxide from local heating. Distillation was carried out in the apparatus shown in Fig. 3, in which the whole system was subjected to intermittent evacuation, not rapid enough to cause excessive foaming. With the first bottle at $+35^{\circ}$ to $+40^{\circ}$ and the condensing U-tube at about -20° it was possible in a couple of hours to condense out 5 to 10 g. of the crude nitrogen

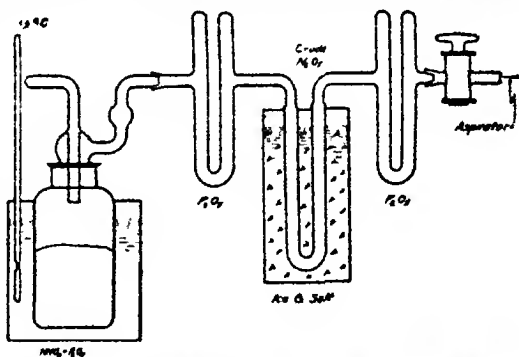


Fig. 3.—Preparation of crude nitrogen pentoxide.

enough to cause excessive foaming. With the first bottle at $+35^{\circ}$ to $+40^{\circ}$ and the condensing U-tube at about -20° it was possible in a couple of hours to condense out 5 to 10 g. of the crude nitrogen

¹ Ladenburg and Lehman, *Verh. deut. physik. Ges.*, 8, 20 (1906); Johnson, *Z. physik. Chem.*, 61, 457 (1907); Bodenstein, *Z. Elektrochem.*, 15, 244 (1909); Preuner, *Z. physik. Chem.*, 82, 129 (1913); Gibson, *Proc. Roy. Soc. (Edinburgh)*, 33, 1 (1913); Baumé and Robert, *Compt. rend.*, 168, 1199 (1919).

² Weber, *J. prakt. Chem.*, 6, 342 (1873); Berthelot, *Ann. chim. phys.*, 6, 202 (1875).

³ Monatsh., 34, 1051 (1913).

pentoxide, stained yellow from its partial decomposition into nitrogen peroxide.

The crude product, protected with its drying tubes of phosphorus pentoxide, was next purified by sublimation in a stream of ozonized air which had passed through an ozonizer of the Berthelot type, and condensed in the vapor-pressure apparatus or other receiver, in the manner shown in Fig. 4. The decomposition of nitrogen

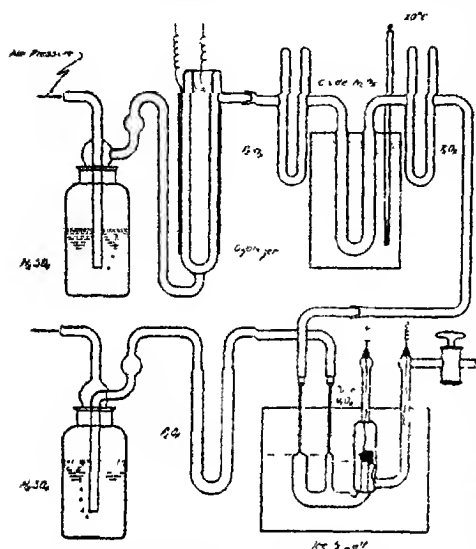


Fig. 4.—Preparation of nitrogen pentoxide.

pentoxide gas into brown fumes of nitrogen tetroxide (and nitrogen peroxide) and oxygen was prevented by an excess of ozone, and pure white crystals could be condensed out under these conditions. Before sublimation all the brown gas was swept out of the apparatus with ozonized air while the crystal tube was still surrounded by ice and salt and the receiver was at room temperature. The receiver was then packed in ice and salt and the crude crystals raised to about 20° , or higher, if the stream of ozone was sufficiently concentrated to prevent all decomposition.

All connections were made with ground-glass joints or with small tubes fitting tightly into larger ones and rendered gas-tight with de Khotinsky cement. The latter was rapidly attacked, however, if appreciable areas were exposed. It was absolutely necessary to exclude every trace of moisture and all leaks had to be guarded against. During the sublimation in ozone, in which operation the greatest care is required, the pressure of the system was always greater than that of the atmosphere so that moist air could not get in.

Some of the nitrogen pentoxide was lost, inasmuch as its vapor pressure at -21° is 7 mm., but this loss was comparatively small since the concentration of the entering gas corresponds to its vapor pressure of 279 mm. at $+20^{\circ}$. Russ and Pokorny¹ recommend the use of solid carbon dioxide for the refrigerating agent and oxygen instead of air to give a higher concentration of ozone. This makes the preparation more diffi-

¹ *Loc. cit.*

cult, but it is necessary in their method, which combines the 2 operations shown in Fig. 3 and Fig. 4 into one operation. The reason for this lies in the fact that the driving out of the nitrogen pentoxide from the semi-solid mass of nitric acid and phosphorus pentoxide, according to their procedure, is a very slow process, and does not permit the attainment of vapor-pressure equilibrium except in a very slow stream of ozone.

Experimental Procedure.

A serious difficulty in the way of accurate determinations of the vapor pressure of nitrogen pentoxide, aside from chemical action on apparatus ordinarily used for such work, lies in the fact that it decomposes rapidly in the gaseous state, giving an abnormally high, and constantly increasing, pressure. In the present research a simple, static method was used in which the rate of decomposition at each temperature was determined and corrected for.

After condensing out about 5 g. of the pure nitrogen pentoxide as shown in Fig. 4, the capillaries were sealed off and the apparatus transferred to a thermostat which was constant to a few hundredths of a degree. Since decomposition was greatly accelerated by light the thermostat was placed in a photographic dark room and connected with the rest of the apparatus shown in Fig. 1, through holes in the wall. After evacuating with a Nelson pump through Stopcock A, Tube D, containing a short collar of glass, was slipped over the end of one of the capillaries and made gas-tight with a little de Khotinsky cement. The pump was started and the tip of the capillary broken off inside the rubber tubing with the help of a pair of forceps. A file scratch previously made facilitated the operation. In this way it was possible to make many successive evacuations with the same crop of crystals without access of the atmosphere at any time.

When the evacuation had continued long enough the capillary was sealed off while the apparatus was in the thermostat. It was necessary to have the capillaries very small so that the volume of gas heated in the process of sealing them off was negligible. In making a pressure reading, air was admitted slowly through Stopcock A, (Fig. 1) until the electrical circuit was broken. The levelling bulb was lowered first by hand and then with the help of the micrometer screw, B, until a throw of the galvanometer was registered. The difference in level between the 2 columns of mercury when electrical connections was just made was always taken as the manometer reading. In case the pressure to be measured was greater than an atmosphere it was necessary to force air under pressure through A.

A typical numerical example shows the method of obtaining the desired pressure values.

Manometer reading with inner compartment open to the atmosphere = 37.0 mm. (zero reading).

Manometer reading when material is sealed off = 661.0 mm.

Barometer = 748.4 mm.

$748.4 - 37.0 - 661.0 = 50.4$ mm. (pressure inside the diaphragm at the temperature of the thermostat).

All the readings of the barometer and manometer were reduced to zero centigrade.

In any static method for determining vapor pressures it is absolutely essential to remove every trace of impurity, for each foreign gas registers its own partial pressure, and the sum of all the pressures is the quantity measured in the experiment. This source of error was eliminated by continued evacuation and evaporation of a large portion of the crystals, in which operation any gas other than nitrogen pentoxide was swept out. In the preliminary experiments there was no criterion for sufficient evacuation except constancy of results after repeated experiments. The time-pressure curves for one temperature were all parallel, but each new one was lower by several millimeters than the preceding curve, until the constant value was reached, after which further evacuation gave no change. It became evident that it was necessary to evaporate a large portion of the crystals, nearly half, before the true vapor pressure could be obtained. The ultimate procedure then consisted in evacuation at or near room temperature until all the crystals had fallen to the bottom of the apparatus, since the proper value was never obtained while crystals were still clinging to the glass walls. A necessary criterion of sufficient evacuation was the "rattling" of the crystals on shaking. In the final experiments, further evacuations rarely showed any lowering of the vapor pressure. After once obtaining the pure material in this way, only a short evacuation was needed after each experiment before starting a new one with the same crop of crystals.

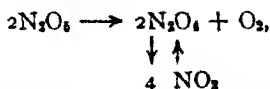
Results.

An examination of the time-pressure curves shown in Fig. 5 is interesting. During the first minute or two after sealing off, the pressure rose rapidly, particularly at the higher temperatures. This rapid rise was due chiefly to the attainment of thermal equilibrium, for although the apparatus was immersed in the thermostat water, the thermal conduction through the glass and the crystals was not sufficient to counterbalance the cooling due to the vaporization of the crystals. The slope of the first part of the curve has no particular significance since it depended on several variables such as the ratio of the quantity of crystals to the total volume 20 cc. and their geometrical arrangement, as well as on the speed of evacuation. The steepest slope possible was desired so that the significant part of the curve, the more horizontal part, due to the decomposition of

gaseous nitrogen pentoxide, would be quickly reached. The shorter this indefinite region the more accurate is the extrapolation to zero time. The extrapolated value gives the true vapor pressure without decomposition.

At the higher temperatures the extrapolation becomes less accurate for 3 reasons: first, the decomposition slope becomes so steep that it is difficult to tell just where it begins and where the slope, due to the attainment of thermal equilibrium, ends; second, the cooling effect from the evaporation of crystals is greater because of the higher vapor pressures, so that the extrapolation has to extend over a longer time interval; third, the decomposition curve is not a straight line.

At the higher temperatures the decomposition curve is not straight for the following reasons. The rate of decomposition of gaseous nitrogen pentoxide depends on its concentration, but this is constant in the presence of the solid phase when the temperature is constant. Accordingly, the decomposition would be represented on the time-pressure diagram as straight lines, except for the fact that as the reaction



proceeds, the partial pressure of the nitrogen tetroxide and peroxide becomes greater, and a shifting of the equilibrium toward nitrogen tetroxide (smaller volume) results. The pressure increase due to the decomposition of a definite number of molecules of nitrogen pentoxide becomes, then, continually smaller. If the experiments were carried out over a sufficiently long time an abrupt change would occur when the partial

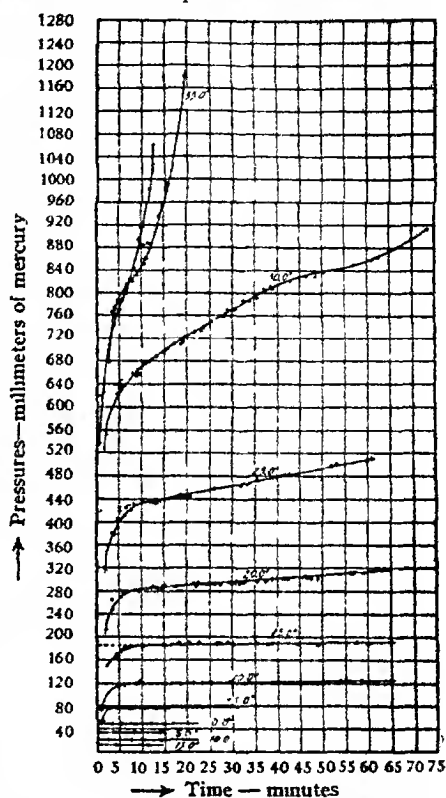


Fig 5—Decomposition of nitrogen pentoxide with solid phase present.

pressure of the nitrogen tetroxide reached a sufficiently high value to give condensation.

At the lower temperature the partial pressure of the nitrogen tetroxide and dioxide is so small even after an hour, that the change due to the equilibrium shift is negligible. Even at 25° and 30°, although a correction for this effect, after an hour amounts to several millimeters, its influence on the extrapolation is not sufficiently great to warrant a correction for it in obtaining the vapor pressures. The rate of decomposition of nitrogen pentoxide will be discussed fully in a later paper.

On the 30.0° curve a change in the slope occurs after about 45 minutes, which is coincident with the first appearance of melting. It is not a true melting, but a phenomenon complicated by the dissolving of nitrogen tetroxide in the surface of the crystals.

The 35.0° curve is of small value in estimating the vapor pressure because the contamination with nitrogen tetroxide and the appearance of melting occurs in the first few minutes. Furthermore, the decomposition curve is so steep that it cannot be distinguished from the curve showing the attainment of thermal equilibrium.

Extrapolation back to zero time for the true vapor pressures, is not entirely legitimate for in so doing it is assumed that the vapor pressure equilibrium is reached immediately after sealing off the capillary, whereas the experiments show that such is not the case. No exact mathematical correction can be made for this error, but it is entirely negligible at the lower temperatures, and even at the higher temperatures remains less than the other errors of extrapolation.

Most of the curves are the average of 3 independent experiments as shown by the representation of points as +, O and ⊙. Each series of these marks represents a fresh evacuation, and many of them were obtained with different crops of crystals. Three different diaphragms were used in the experiments, each with different dimensions and a different zero point.

The true vapor pressures (without decomposition) obtained by extrapolation to zero time are shown in the second column of Table I. In Fig. 6, which gives the vapor pressure-temperature curve they are represented by circles. They check closely with results of Russ and Pokorny,¹ shown in Col. 3, and represented by triangles on the curve. These investigators used a dynamic method, which was not suitable above 8.5° on account of the decomposition of nitrogen pentoxide.

Russ and Pokorny¹ used, for temperatures between 0° and 17.5°, a static method in which ozone prevented the decomposition. These results are shown by crosses in Fig. 6. They are several millimeters higher than the other results. In discussing the discrepancy between their two

¹ *Monatsh.*, 34, 1027 (1913).

methods, Russ and Pokorny placed reliance in the dynamic method and concluded that the crystals used in their static method were contaminated with traces of nitric acid. The experience gained in the present research supports this conclusion and shows further that the last traces of foreign gases can be eliminated only by long evacuation and evaporation of a large portion of the crystals.

Using the results obtained by their dynamic method, Russ and Pokorny derived the following equation, based on the Nernst vapor pressure formula, to show the relation between temperature and the vapor pressure of nitrogen pentoxide.

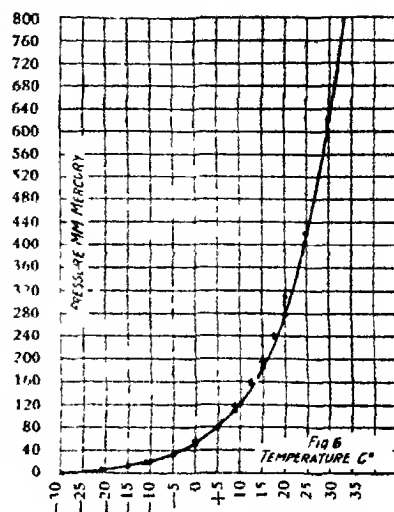


Fig 6—Vapor pressure of nitrogen pentoxide.

$$\log P = \frac{-3161.2}{T} + 1.75 \log T - 0.00606 T + 10\,679.$$

The values calculated from this equation are shown in Col. 4 of Table I. For pressures below a quarter of an atmosphere it is very satisfactory, but it is only approximate for higher pressures.

For a whole range of vapor pressures up to one atmosphere the following *empirical* equation is superior.

$$\log P_{\text{mm}} = \frac{1244}{T} + 34.1 \log T - 85\,929.$$

The figures given in Col. 5 of Table I are calculated from it.

The vapor pressure reaches an atmosphere at 32.5° , as shown by a short extrapolation of the curve. The melting point lies above the sublimation point, as stated by Russ and Pokorny.¹ Liquid nitrogen pentoxide, referred to in the older literature, must have been contaminated with moisture from the atmosphere. The solid nitrogen pentoxide forms clear and perfect hexagonal prisms, growing to a length of several millimeters on long standing at 0° .

The heats of sublimation as calculated by the Clausius-Clapeyron equation $\left(L = 2\,303 R \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1} \right)$ are given in Table II. P_1 and P_2 in each case represent the vapor pressure at 5° above and 5° below the temperature for which the heat of sublimation, L , is calculated. The

¹ *Loc. cit.*

FARRINGTON DANIELS AND ARTHUR C. BRIGHT.

TABLE I.—VAPOR PRESSURE OF NITROGEN PENTOXIDE.

1. Temp. ° A.	2. Observed. Daniels & Bright. Static method. Mm.	3. Observed Russ & Pokorny. Dynamic method Mm.	4. Calculated Russ & Pokorny. $\log P = -3161.2/T$ $+ 1.75 \log T -$ $0.00606 T + 10.679$ Mm.	5. Calculated. Daniels & Bright. $\log P = 1244/T +$ $34.1 \log T - 85.929$ Mm.
243.0	...	2.3	2 3	3.5
246.5	...	3.3	3 4	4.8
252.0	...	6 3	6.5	7.8
258.0	13	...	12 4	13.5
262.3	...	18.6	18.7	19.7
263.0	21	...	19 9	21 0
268.0	32	...	32 3	32.5
273.0	51	51 5	51.1	50.2
278.0	79	...	79 7	77.3
281.7	...	111 2	109.4	106
283.0	118	...	121.5	118
283.5	...	132	126 7	125
288.0	183	...	183	181
293.0	279	...	270	275
298.0	420	...	390	414
303 0	620	...	566	622
305.5	760	.	674	762

results at the lower temperatures are not accurate because the experimental error of one mm. is large compared with the total vapor pressure. At the higher temperatures, also the results are less accurate on account of the large error of extrapolation of the decomposition curves. It is evident from the table that the heat of sublimation, as calculated, increases with the temperature, but the experimental error is magnified to such an extent in the calculations that the exact value of the temperature coefficient is in doubt.

TABLE II.

Temperature ° A.	Heat of sublimation. Calories.
263	12,360
268	12,640
273	12,760
278	13,110
283	13,360
288	14,160
293	14,140
298	14,040
305.5 (extrapolated)	14,970

The results agree within the limit of experimental error with those calculated from the results of Russ and Pokorny.¹ Berthelot² found the heat of sublimation of nitrogen pentoxide at 10° to be 13,100 calories by calorimetric experiments. This checks satisfactorily with the value 13,360 calories, as shown in the table.

¹ *Loc. cit.*

² *Ann. chim. phys.*, 6, 151 (1875).

Summary.

1. A new all-glass manometer has been devised in which a platinized glass diaphragm is arranged to close an electrical indicating circuit. A measured air pressure was thus balanced against the unknown pressure, without the aid of optical systems.

2. A convenient method for preparing pure nitrogen pentoxide has been described.

3. The vapor pressures of nitrogen pentoxide have been determined by a static method in which corrections were made for the decomposition occurring in the gaseous phase. The results agree at the lower temperatures with those of Russ and Pokorny obtained by a different method, and extend to higher temperatures than they were able to employ. The vapor pressures of nitrogen pentoxide are conveniently given by the empirical formula:

$$\text{Log } P_{\text{mm}} = \frac{1244}{T} + 34.1 \log T - 85.929.$$

4. The sublimation point and heats of sublimation of solid nitrogen pentoxide have been calculated.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY,
No. 334]

ADDITION COMPOUNDS OF AMMONIA WITH THE AMMONIUM HALIDES.

BY JAMES KENDALL AND J. G. DAVIDSON.

Received March 23, 1920.

The fact has long been noted in the literature¹ that the majority of the salts of ammonium are exceptionally soluble in anhydrous liquid ammonia, and a great deal of work has been done in the examination of the nature of such solutions. The most familiar case is that of ammonium nitrate, which absorbs ammonia readily at ordinary temperatures to form a mobile liquid known as Divers' solution.² Conflicting conclusions have been drawn regarding this system by different investigators. Raoult³ deduced the existence of compounds of the formulas NH_4NO_3 , 2NH_3 , and $\text{NH}_4\text{NO}_3 \cdot \text{NH}_3$; Troost⁴ claimed to have obtained 2 different compounds; $2\text{NH}_4\text{NO}_3 \cdot 3\text{NH}_3$, and $\text{NH}_4\text{NO}_3 \cdot 3\text{NH}_3$; while Kuriloff,⁵ who first established the complete freezing point diagram, isolated only the latter compound— $\text{NH}_4\text{NO}_3 \cdot 3\text{NH}_3$ —which showed a m. p. of -40° .

¹ See Franklin and Kraus, *Am. Chem. J.*, 20, 820 (1898).

² Divers, *Proc. Roy. Soc.*, 21A, 109 (1873).

³ Raoult, *Compt. rend.*, 76, 1261 (1873).

⁴ Troost, *ibid.*, 94, 789 (1882).

⁵ Kuriloff, *Z. physik. Chem.*, 25, 107 (1898).

Ammonium thiocyanate is also extremely deliquescent in ammonia. Bradley and Alexander¹ have succeeded in obtaining a whole series of addition compounds in this system, further data regarding which have recently been published by Foote and Hunter.²

For the remaining salts few results of any value are available. Troost³ has stated that ammonium chloride forms with ammonia the compounds $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$ (m. p. $+7^\circ$) and $\text{NH}_4\text{Cl} \cdot 6\text{NH}_3$ (m. p., -18°). Ammonium bromide and ammonia have been investigated by Troost⁴ and Roozeboom;⁵ compounds of the formulas $\text{NH}_4\text{Br} \cdot \text{NH}_3$; $\text{NH}_4\text{Br} \cdot 3\text{NH}_3$ (m. p., $+8.7^\circ$) and $\text{NH}_4\text{Br} \cdot 6\text{NH}_3$ (m. p., -20°) have been deduced.

In the present article the results of an examination of the freezing-point curves of ammonium chloride, bromide and iodide with ammonia over the whole of the available concentration range are recorded. Ammonium fluoride was found to be practically insoluble in liquid ammonia⁶ and to form no compounds. The curve for the system $\text{NH}_4\text{NO}_3\text{--NH}_3$ was also redetermined in part, but since the data of Kuriloff were duplicated within the limits of experimental error, the results need not be repeated here.

Experimental.

The whole work was carried out in sealed glass bulbs, as described by Smith and Eastlack.⁷ Anhydrous ammonia was obtained by warming a concentrated aqueous solution, drying the gas given off by means of quicklime and fused potassium hydroxide, and condensing in a tube surrounded by liquid air. The salts were c. p. products, recrystallized before use.

Mixtures of known composition were made by adding liquid ammonia to a weighed quantity of the powdered salt in an unsealed bulb, sealing at once and weighing again. A handle was fused to the bulb and complete admixture of its contents brought about by warming and shaking. Solidification was induced by rapid cooling in liquid air and the bulb, with a thermometer, was then immersed in a bath, the temperature of which was slowly raised until the point of disappearance of the last few crystals was noted. By careful repetition of this procedure the exact freezing point of the mixture was obtained.

Below 0° the bath employed was an unsilvered Dewar flask containing alcohol previously cooled by liquid air. Above 0° a water bath was substituted. For temperatures below -35° a toluene thermometer was used, standardized at the freezing points of mercury and pure ethyl

¹ Bradley and Alexander, *THIS JOURNAL*, 34, 15 (1912)

² Foote and Hunter, *ibid.*, 42, 69 (1920)

³ Troost, *Compt. rend.*, 88, 578 (1879)

⁴ Troost, *ibid.*, 92, 715 (1881).

⁵ Roozeboom, *Z. physik. Chem.*, 2, 460 (1888)

⁶ Compare Franklin and Kraus, *loc. cit.*

⁷ Smith and Eastlack, *THIS JOURNAL*, 38, 1262 (1916).

acetate.¹ Above -35° a standardized mercury thermometer was employed. The freezing points recorded below may be regarded as of the following accuracy: from -80 to -35° , possible error 0.5° to 1.0° , above -35° , possible error 0.2° to 0.5° .

It was found impossible to carry the curves much above ordinary temperatures owing to the enormous ammonia pressures there exerted. Persistent efforts to obtain more points merely resulted in the sudden transference of the apparatus to the ceiling of the laboratory. However, since in all cases the neutral salt had already been reached as solid phase, no compounds have been missed by this incomplete examination of the systems.

The results obtained are given in the tables below and in the accompanying diagram. The significance of the curves need not be elaborated upon here; it is sufficient to state that each break indicates a change in solid phase and that the composition of each compound isolated is automatically determined by its maximum point on the curve.

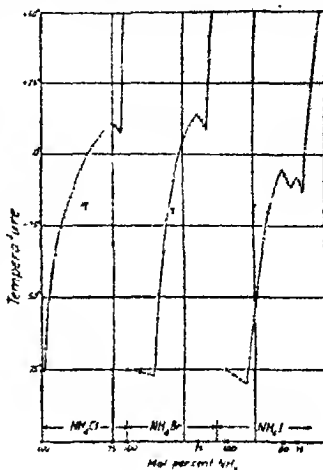


Fig. 1.

Ammonia Ammonium Chloride:

(a) Solid phase, NH_3

Mol % NH_3	100
T	-74.8

(b) Solid phase, $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$

Mol % NH_3	98.8	97.4	95.5	93.1	92.2	91.3	89.8	88.6	87.9
T	-67.4	-50.5	-35.0	-25.6	-22.0	-19.6	-15.0	-11.9	-10.0
Mol % NH_4Cl	86.0	83.0	81.9	79.0	77.1	75.0	74.0		
T	-5.1	0.0	3.2	6.6	9.5	10.7	10.0		

(c) Solid phase, NH_4Cl

Mol % NH_3	72.3	71.5
T	9.1	31.0

Ammonia Ammonium Bromide:

(a) Solid phase, NH_3

Mol % NH_3	100	95.6	92.9
T	-74.8	-76.0	-76.7

(b) Solid phase, $\text{NH}_4\text{Br} \cdot 3\text{NH}_3$

Mol % NH_3	89.5	88.9	87.6	85.9	83.4	82.4	81.3	79.7
T	-57.4	-49.0	-34.0	-23.1	-9.0	-4.1	0.4	6.0
Mol % NH_4Br	77.8	76.2	75.0	74.3	73.1	72.8	72.2	
T	10.1	12.1	13.7	13.1	11.7	10.9	9.7	

¹ Compare Kendall and Booge, *THIS JOURNAL*, 38, 1718 (1916)

(c) Solid phase, NH_4Br .

Mol. % NH_3 ...	71.8	71.4	70.7	69.9	68.6
T.....	9.2	20.0	32.6	53.0	87.0

Ammonia-Ammonium Iodide:(a) Solid phase, NH_4I .

Mol. % NH_3 ...	100	97.5	95.4
T.....	-74.8	-76.8	-78.6

(b) Solid phase, $\text{NH}_4\text{I} \cdot 4\text{NH}_3$.

Mol. % NH_3 ...	92.8	92.0	90.2	88.8	86.8	85.1	84.0
T.....	-79.5	-71.0	-58.0	-46.2	-29.5	-20.2	-16.0
Mol. % NH_3 ...	83.2	82.0	80.0	79.2	77.9	77.0	
T.....	-13.2	-9.4	-5.1	-6.8	-9.2	-10.9	

(c) Solid phase, $\text{NH}_4\text{I} \cdot 3\text{NH}_3$.

Mol. % NH_3 ...	76.9	75.9	75.0	74.3	73.8	73.2
T.....	-10.9	-9.1	-8.0	-8.9	-10.0	-11.5

(d) Solid phase, NH_4I .

Mol. % NH_3 ...	72.4	71.5	69.8	68.0	66.8
T.....	-7.0	2.5	22.6	44.2	57.0

Discussion of Results.—From the diagram it will be seen that the existence of the following compounds has been demonstrated:

	M. p.
(a) $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$	10.7°
(b) $\text{NH}_4\text{Br} \cdot 3\text{NH}_3$	13.7°
(c) $\text{NH}_4\text{I} \cdot 3\text{NH}_3$	-8.0°
(d) $\text{NH}_4\text{I} \cdot 4\text{NH}_3$	-5.1°

The melting points of the first 2 of these compounds are considerably higher than the values recorded by previous workers. The other 2 compounds have not been isolated before.

No evidence was obtained in support of the compounds, $\text{NH}_4\text{Cl} \cdot 6\text{NH}_3$ and $\text{NH}_4\text{Br} \cdot 6\text{NH}_3$, claimed by Troost.¹ From the position of the melting points given by him for these compounds, as referred to the general curves (see the 2 points marked T in the diagram), it appears that their existence is extremely improbable. In the same way no indication was given of compounds of the type $\text{NH}_4\text{Br} \cdot \text{NH}_3$. While no actual analyses were carried out upon the solid phases separating out at ordinary temperatures from the mixtures, yet their crystal habit was in each case identical with that of the neutral salt.

When we compare the curves among themselves, we note a regular increase in the extent and stability of compound formation as we pass upwards through the series of halogens. Ammonium fluoride forms no compounds at all with ammonia. The chloride forms a compound $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$, which is appreciably dissociated into its components on fusion, as is shown by the relative flatness of the curve in the region of its maximum. The compound $\text{NH}_4\text{Br} \cdot 3\text{NH}_3$ is much more stable, as may be seen by the

¹ Troost, *loc. cit.*

sharper maximum on the diagram. With ammonium iodide, finally, not only is there obtained a stable compound of the regular type, $\text{NH}_4\text{I} \cdot 3\text{NH}_3$, but also a second very stable compound of the composition $\text{NH}_4\text{I} \cdot 4\text{NH}_3$.

The stability of these compounds, indeed, is so unexpectedly high that it is evident that their existence at higher temperatures and even in the vapor phase cannot be entirely left out of consideration in any exact study of the ammonium halides. For example, Smith and Lombard¹ have found that the vapor density of ammonium iodide at temperatures below 350° is greater than the value required by the formula NH_4I , and have suggested that any dissociation into ammonia and hydrogen iodide is outbalanced by association into complex molecules of the type $(\text{NH}_4\text{I})_x$. The present investigation indicates an alternative and very plausible explanation, namely that complex molecules of the type $\text{NH}_4\text{I} \cdot n\text{NH}_3$ (and perhaps, too, of the type $\text{NH}_4\text{I} \cdot n\text{HI}$, since ammonium nitrate has been shown by Ditte² and by Groschuff³ to form stable addition compounds with nitric acid) are existent in the vapor phase, raising the observed density above the normal value. The possibility of the presence of such compounds in the vapor phase also adds a new complication to the discussion between Wegscheider⁴ and Smith⁵ on the abnormalities in the vapor densities of dried and undried ammonium chloride.

Summary.

The freezing point curves of the ammonium halides with ammonia have been determined throughout the whole available composition range.

Compounds of the following formulas have been isolated: $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$ (m. p., 10.7°), $\text{NH}_4\text{Br} \cdot 3\text{NH}_3$ (m. p., 13.7°); $\text{NH}_4\text{I} \cdot 3\text{NH}_3$ (m. p., -8.0°); $\text{NH}_4\text{I} \cdot 4\text{NH}_3$ (m. p., -5.1°). Other compounds of these systems previously recorded in the literature are probably non-existent.

The stability of the addition compounds with ammonia increases regularly as we ascend the series of the ammonium halides. Some consequences of the probable persistence of these compounds in the vapor phase have been briefly indicated.

NEW YORK, N. Y.

¹ Smith and Lombard, *THIS JOURNAL*, 37, 66 (1915).

² Ditte, *Ann. chim. phys.*, 18, 320 (1879).

³ Groschuff, *Ber.*, 37, 1486 (1904).

⁴ Wegscheider, *Z. anorg. Chem.*, 103, 207 (1918).

⁵ Smith, Eastlack and Scatchard, *THIS JOURNAL*, 41, 1961 (1919).

[COMMUNICATION FROM THE RESEARCH DIVISION, C. W. S., AND THE FIXED NITROGEN RESEARCH LABORATORY]

THE HEAT OF ABSORPTION OF VAPORS ON CHARCOAL.¹

BY ARTHUR B. LAMB AND A. SPRAGUE COOLIDGE.

Received March 28, 1920.

Introduction.

In the study of the properties of active charcoal for use in gas masks it appeared of importance to determine the adsorption isotherms of a large variety of vapors upon charcoal, and the quantity of heat thereby evolved. It was soon found that the precise adjustment of adsorption pressure equilibria is very slow and exhibits irregularities apparently connected with the presence in the charcoal of minute traces of air and other impurities. The study of this aspect of the problem was, therefore, postponed, and attention was directed chiefly to the study of the amounts of heat evolved during adsorption.

In these thermal measurements complete adjustment of the adsorption equilibrium is also slow, but at least at low pressures, the greater portion of the gas is taken up in a few minutes, so that accurate calorimetric measurements can be made quite rapidly by a suitable method as, for instance, that using the ice-calorimeter, provided the gradual adsorption of the remaining vapor by the charcoal be prevented. This can be done by closing off the system after an appropriate interval, close to the charcoal. The little residual vapor thus entrapped, even if it were completely adsorbed, could not evolve a measurable quantity of heat.

Our general method of procedure was to enclose in a glass tube, a weighed quantity of charcoal freed from gaseous impurities by evacuation at a high temperature, place this tube in an ice-calorimeter, and when constant readings had been obtained, to introduce a measured quantity of the vapor in question at low pressure into the tube. We waited until most of it had been adsorbed, then shut the residual gas off from the charcoal, and finally observed the stationary reading of the ice-calorimeter. This process could be repeated with fresh samples until an equilibrium pressure had been attained beyond which it was impossible to go without condensation of the vapor at 0°. Similar measurements using an ice-calorimeter have previously been made on nitrogen, carbon dioxide and ammonia by Titoff.²

The apparatus, materials and experimental procedure are first described; the results obtained and a discussion of them follow.

¹ Published by permission of Maj Gen W. L. Sibert, Director, C. W. S., U. S. Army

² The authors wish gratefully to acknowledge their indebtedness to Margaret S. Coolidge for her skilful execution of a number of the measurements recorded in this paper

³ *Z. physik. Chem*, 74, 641 (1910).

Apparatus.

The apparatus used in these measurements presents certain advantages as compared with that used by Titoff; it is shown in Fig. 1. It consists essentially of the bulb A in which the gas or vapor is stored; the manometer B; the ice-calorimeter C, and the valve D.

The bulb A, together with the connecting tubes and the parts of the manometer and valve which are occupied by gas, constitute the volume used in calculating the quantity of gas adsorbed. The temperature of the greater part of the system is given by that of the water at room temperature which surrounds A; that of the small volume represented by the valve, manometer, and connections, will not differ sufficiently to cause appreciable error.¹

B serves as a manometer, and also as a valve to isolate the system from the pump (a Gaede mercury pump) so that the latter may be stopped or used for other purposes. The small side-tube *a* can be used as a simple MacLeod gage to indicate the vacuum attained. A cathetometer is used to read the manometer, and since it can be relied on to only 0.05 mm., it is not necessary to employ refined methods of measuring the vacuum. We have

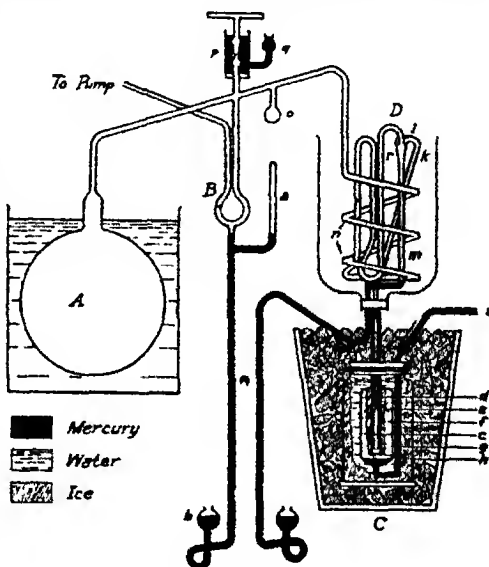


Fig. 1.— Adsorption apparatus and ice-calorimeter.

not used a permanently exhausted manometer, because of the difficulty of cleaning and refilling. The one we used can be easily cleaned by emptying the mercury through *b* and pouring in cleaning solution by means of a funnel inserted through the filling plug *p*.

The sample of charcoal is contained in the small bulb *c*, which can be inserted in an ice-calorimeter of the usual design. The latter is protected from heat exchange by immersion in a glass jar containing distilled water

¹ In a later form of apparatus, the large bulb was inverted and the connecting tubes all sloped to drain into B or D. This was a great improvement, as mercury is certain sooner or later to fly about in the apparatus, but with this arrangement it all runs out again. In the old apparatus there was usually a little puddle of mercury in A, whose volume had to be estimated and corrected for, and which could be removed only by taking the apparatus apart.

and lined with pure ice by previous immersion in a freezing mixture. The addition of 2 drops of alcohol to the water in the jar serves to balance the depression of the freezing point of the water in the calorimeter due to the pressure of the mercury in the leading-out tube, and we have no correction for heat exchange. This probably has no advantage over a small constant heat exchange so far as accuracy is concerned, but is much more convenient, as it is unnecessary to record the time accurately and then to calculate the correction. In the diagram, *d* is the inside tube of the calorimeter, surrounded by the sheath of ice *e*; *f* is the calorimeter jacket, *g* the protective coating of ice on the inside of the jar *h*. Heat is conducted from *c* to *d* by the water which fills the space between them up to a point just below the top of the ice sheath. The whole is packed in a tub of crushed ice, and mounted on an adjustable platform by means of which it can be run under the charcoal tube and raised into position.

The ice-calorimeter is read by a capillary tube *i* inserted through the cork sleeve; one millimeter of the scale used in calibrating corresponded to 0.589 cal. at 15°. This constant was determined by dropping in known weights of water and glass previously brought to constant room temperature. The bulb used weighed 2.986 g. and the specific heat of its glass, separately determined, was 0.189. The bulb contained 2.730 g. of water of average specific heat of 1.004, making the total heat capacity of the filled bulb 3.304 cal. Four separate experiments gave values varying between 0.587 and 0.590 cal. per mm. of the scale, with a mean value of 0.589.

Ostwald¹ gives 1.546 g. of Hg per cal.; since 75.1 mm. of this capillary contained 0.6835 g. of Hg this corresponds to 0.5885 cal. per mm.

The capillary tube used in the present experiment was somewhat smaller than the above, and its constant, found by weighing a column of mercury, was 0.587 cal. per mm. There were also small corrections for variations in its bore, amounting to between -0.1 and $+0.1$ mm. which were determined and applied.

The admission of the gas to the charcoal is controlled by the mercury valve D. When the level of the mercury is lowered, gas enters the charcoal tube through *k*, while the trap *l* separates any mercury carried over and returns it through *m*. N is a spiral glass tube which is immersed in ice and water after the pressure of the gas has been read, but before it is admitted to the charcoal. This insures that the entering gas will not carry in any extraneous heat.² The arrangement designed to make

¹ Ostwald-Luther, "Hand-und Hilfsbuch," 3rd Ed., p. 334.

² The apparatus was so arranged that the principal drop in pressure between the reservoir and the charcoal occurred inside the calorimeter. An approximate computation demonstrated that neither the kinetic energy of the inflowing gas nor the Joule-Thomson effect could have produced any significant error.

as small as possible the space in connection with the charcoal after the valve has been closed, since with a large dead space the gradual adsorption of small quantities of gas would continue for some hours, and a definite reading would be difficult to obtain. Some of the gases studied condense at the pressures used when the temperature is reduced to zero. It was feared that if this were allowed to occur in the valve, the gas on re-evaporating might be cooled and enter the calorimeter below the freezing point. To prevent this, a bulb *o* is provided; by immersing this in ice and water, the gas can be condensed there and the pressure so lowered that no further condensation occurs when *D* is subsequently cooled. Naturally, this is not done till the pressure and temperature of the gas have been ascertained.

The substance under examination is admitted to the system through the filling plug *p*. This is not lubricated, but is ground at an angle large enough to prevent sticking. It is normally covered with mercury, and is perfectly tight when so sealed. When it is in a certain position, a scratch on the upper half of the socket meets one on the lower half of the plug, forming a very narrow channel. In filling, liquid is poured on top of the mercury forming the seal, which is then lowered until the top of the grinding is covered with the liquid. The plug is then turned, and the liquid flows in through the scratch until the desired pressure has been attained, when the plug is again turned and the mercury seal replaced. It is generally necessary to boil away the superfluous liquid, as otherwise its capillary properties enable it to creep under the mercury seal and through the grinding, causing the pressure in the apparatus to increase slowly. When the plug is dry, the pressure remains constant indefinitely. This plug is more satisfactory than any other device we have thought or read of, as it does not depend on lubricants, which are rapidly attacked by some of the substances examined, nor on sweeping out the air in an intermediate chamber, which is uncertain, wasteful of material, and involves filling the pumps with liquids which may dissolve in the oil of the backing pump and be removed with difficulty.

Materials.

All the liquids used were carefully purified by appropriate chemical treatment, and were fractionated in a glass still with an efficient still-head until the main portion came over within a few hundredths of a degree. All liquids were used immediately after preparation.

The charcoal used in all but a few of the measurements was from one lot of a steam-activated coconut charcoal of excellent quality, as shown by the following service time tests made according to the standard C. W. S. accelerated chloropicrin tube-test method.

When allowed to stand overnight in the tubes the tested samples showed 6 minutes recuperative run to the break.

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Weight G.	Temperature, °C.	Pressure drop, Mm. H ₂ O.	Time Min.
8.59	29	33	48.6
8.51	29	31	49.6
<hr/>			
Average, 8.55	29	32	49.1

A few measurements were made with a less active charcoal (E-622). This charcoal was also a cocoanut charcoal of the same mesh as the above and had been activated in a similar way. It ran only 14.4 minutes when tested according to the same procedure. It is referred to in what follows as "inactive" charcoal.

Method of Experimentation.

Preliminary Treatment of the Charcoal.—The tube in which the charcoal is to be contained is first sealed to one part of a ground glass connection and weighed. It is then filled with charcoal, attached to the Gaede pump by the ground joint, and evacuated for an hour and a half at 350°, and at a pressure of 0.01 mm,¹ the heating being accomplished by a small electric tube furnace. While still hot and evacuated, the bulb is sealed off, and when cool is weighed together with the original part of the ground joint, so that exactly the same portions of glass figure in each weighing, and the difference is the charcoal taken, freed from adsorbed gases and moisture. The charcoal tube is now sealed to the apparatus in the proper place, and again heated and exhausted for an hour, after which the valves are closed, the charcoal tube cooled in ice, and the calorimeter placed in position. It requires half an hour for the latter to come to equilibrium.

Introduction of the Gas.—While the charcoal is cooling, gas is introduced through the filling plug, its temperature and pressure read, and, if necessary, it is partially condensed in *c*. When the calorimeter readings have become constant, ice and water are placed around the valve, which is then opened, allowing the gas to flow into the charcoal. After a few minutes, the valve is closed again, the pressure of the gas remaining in the system noted, and the calorimeter watched until its readings become constant. The pressure in the charcoal tube may be compared with that in the main volume at *r*, which, with the volume of dead space, gives the quantity of gas removed from the main volume but not adsorbed by the charcoal. This is generally negligible. This pressure in the bulb at the end of an experiment is not in general the true equilibrium pressure, which may require hours and sometimes days to be established, but in a carefully prepared and unpoisoned charcoal differs but little from it. Another portion of gas is now admitted to the charcoal and the heat measured; this is repeated until the final pressure in the tube reaches or

¹ Since the heat of adsorption was found to be nearly independent of the amount already adsorbed it would seem that a small amount of residual gas could hardly be of much importance.

exceeds 20 mm. These consecutive "experiments" constitute a "run" according to our nomenclature. The charcoal may be heated and evacuated and another run made, either with the same or with a different substance. All the runs made with one sample of charcoal constitute a "series."

Calculation of Results.

Results are expressed in 15° calories and cubic centimeters of gas at normal temperature and pressure, per gram of gas-free adsorbing charcoal. In calculating the gas volumes, a correction representing the effect of molecular attraction is first added to the observed pressure. This is obtained from the values of the constant a of Van der Waals' equation (Landolt-Bornstein), and as a rule amounts to about 0.3% (The effect of the volume of the molecules is negligible at these pressures). The resulting ideal pressure is then used to reduce the volume to 0° and 760 mm, according to the laws of an ideal gas. The complete calculation of an experiment is as follows:

Weight of charcoal sealed in tube, exhausted	19.287 g
Minus weight of glass	15.909 g
Plus weight of displaced air 6 cc	0.007 g
	<hr/>
True weight of charcoal	3.385
Volume of system	1187 cc
Temperature	22.0°
Pressure before adsorption	77.3 mm
Correction for attraction Van der Waals	0.2 mm
Pressure after adsorption	1.9 mm
Pressure drop	75.6 mm
Gas removed,	
$1187 \times \frac{273.0}{295.0} \times \frac{75.6}{760}$	109.3 cc at NTP
Pressure in charcoal tube at end	1.5 mm
Volume of same	12.0 cc
Gas removed but not adsorbed	0.1 cc
Gas adsorbed	109.3 cc at NTP
Ditto per gram charcoal λ'	32.30 cc at NTP
Reading of calorimeter initial	0.0 mm
Ditto, final	126.7 mm
Heat evolved 126.7×0.587	74.4 cal
Heat evolved per gram charcoal, " h "	21.98 cal

The results of each experiment are added to those of all preceding experiments of the same run, thus giving the total gas in the charcoal, λ , and the total heat evolved during its adsorption, h .

The Results.

All the results which we recorded are reported in the following tables. They are also shown in the accompanying Figs. 2, 3 and 4. Three of the results, however, which are bracketed in the tables as obviously wild, are omitted from the plots because it would not be clear to which curve they belong.

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TABLE I.—HEAT OF ADSORPTION MEASUREMENTS ON ACTIVE CHARCOAL.

Carbon Tetrachloride.					
$h = 0.893 \times 10^{10}$.					
Charcoal and run.	Adsorbed gas, π cc.	Heat evolved, h .		Difference, Δ cal.	Pressure, mm.
		Observed, cal.	Computed, cal.		
L ₂	23.56	16.87	16.86	+0.01	..
B ₁	30.35	21.47	21.35	+0.12	..
D ₁	33.50	23.46	23.40	+0.06	..
C ₂	34.91	24.30	24.31	-0.01	..
A ₁	39.50	26.61	27.27	-0.66	..
B ₁	60.94	41.71	40.82	+0.89	4
	76.4	7
A ₁	78.32	51.53	51.55	-0.02	10
R ₁	78.80	51.40	51.83	-0.43	..
	91	21
	108	46

C₂ Used for ether. Exhausted 90 minutes.

A₁ Fresh. Exhausted overnight.

B₁ Same.

D₁ Fresh. Exhausted 2 hours.

L₂ Used for methyl alcohol.

Ether.					
$h = 0.917 \times 10^{12.5}$					
I ₁	18.10	13.39	13.21	+0.18	..
C ₁	35.00	24.15	24.29	-0.14	..
I ₁	37.68	26.06	25.98	+0.08	..
C ₂	43.18	29.45	29.48	-0.03	3
I ₁	58.07	39.06	38.70	+0.36	..
C ₂	75.68	49.31	49.40	-0.09	..
C ₁	78.76	51.40	51.29	+0.11	..
	81.7	10
I ₁	86.77	53.78	56.07	(-2.29)	10
I ₁	99.34	60.61	63.48	(-2.87)	63

C₁ Exhausted 90 minutes.

C₂ Same.

I₁ Fresh. Heated overnight at low pressure, and in vacuum one hour.

Chloroform.					
$h = 0.8295 \times 10^{12.5}$					
J ₁	22.30	14.91	15.11	-0.20	..
H ₁	30.89	20.28	20.40	-0.12	..
G ₁	32.69	21.88	21.59	+0.29	..
J ₁	45.49	29.41	29.40	+0.01	..
H ₁	60.49	38.09	38.40	-0.31	..
G ₁	68.66	43.20	43.21	-0.01	..
H ₁	78.36	48.84	48.90	-0.06	7
	104	15
G ₁	107.10	65.67	68.50	+0.17	..

G₁

H₁ All fresh samples.

J₁ "

TABLE I (continued).

Ethyl Formate.

$$h = 0.944 x^{0.1075}.$$

Heat evolved, h .

Charcoal and run.	Absorbed gas. x cc.	Observed. cal.	Computed. cal.	Difference. Δ cal.	Pressure mm.
P ₂	20.72	15.07	14.79	+0.26	..
P ₁	32.30	21.97	22.11	-0.14	..
P ₂	53.77	35.10	35.12	-0.02	..
P ₁	62.88	40.27	40.47	-0.20	..
P ₂	80.02	50.39	50.37	+0.02	3
P ₁	96.73	59.70	59.83	-0.13	10
P ₁	120.15	73.00	72.87	+0.13	35

P₁ Fresh.P₂ Same.

Carbon Disulfide.

$$h = 0.7525 x^{0.1105}.$$

Z ₂	23.91	13.93	13.99	-0.06	..
Z ₂	38.07	21.82	21.45	+0.37	..
Z ₂	48.40	26.71	26.76	-0.05	..
E ₁	66.58	35.60	35.81	-0.21	6
Z ₁	70.02	37.63	37.59	+0.04	..
Z ₂	74.92	40.19	40.00	+0.19	..
Z ₂	97.94	51.41	51.19	+0.22	3
Z ₂	111.98	58.13	57.92	+0.21	7
Z ₂	127.67	65.40	65.36	-0.04	12
E ₁	128.28	65.25	65.61	-0.36	24
Z ₂	137.78	69.90	70.11	-0.21	15
Z ₂	143.37	69.19	72.73	(-2.55)	21
Z ₂	153.19	76.87	77.27	-0.40	40

Z₂ Used for CS₂. Exhausted overnight.Z₂ Same.E₁ Fresh. Heated at low pressure over night, and in vacuum 2 hours.

Methyl Alcohol.

$$h = 0.742 x^{0.100}.$$

S ₁	21.67	13.39	13.30	+0.09	..
S ₁	47.42	27.64	27.71	-0.07	..
S ₁	75.27	42.76	42.24	+0.02	..
S ₁	103.27	57.44	57.48	-0.04	13
S ₁	127.40	70.08	69.98	+0.10	18

S₁ Fresh. After 2nd expt. the charcoal tube was removed from calorimeter, and allowed to stand in the air overnight. Next morning the run was continued.

Ethyl Chloride.

$$h = 0.7385 x^{0.110}.$$

U ₂	29.10	16.05	16.14	-0.09	..
U ₂	42.66	23.02	22.90	+0.12	..
U ₂	67.01	34.78	34.62	+0.16	..
U ₂	102.81	51.21	51.21	15
U ₂	124.80	61.03	61.17	-0.14	32

U₂ Used for benzene.U₂ Same sample.

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TABLE I (continued).

Ethyl Bromide					
$h = 0.900 \times 10^{100}$					
Charcoal and run	Adsorbed gas, x cc	Heat evolved, h		Difference Δ cal	Pressure mm
		Observed cal	Computed cal		
W ₁	48 90	29 85	29 83	+0 02	
Y ₂	34 10	32 65	32 67	-0 02	
W ₁	91 73	52 55	52 54	+0 01	10
W ₁	120 48	67 15	67 13	+0 02	37

Y₂ Previously used with ethyl alcohol

W₁ Fresh

Ethyl Iodide					
$h = 0.737 \times 10^{100}$					
U ₄	34 42	21 71	21 72	-0 01	
U ₄	67 52	41 40	41 36	+0 04	2
U ₄	99 17	59 97	59 77	+0 20	5
U ₄	124 72	74 11	74 10	-0 28	39

U₄ Previously used with ethyl chloride

Benzene					
$h = 0.774 \times 10^{100}$					
U ₁	28 37	19 16	19 17	0 01	
U ₁	54 70	35 90	35 93	-0 03	2
U ₁	81 03	52 51	52 39	+0 15	3
U ₁	102 04	65 30	65 34	-0 04	13

U₁ Fresh

Ethyl Alcohol					
$h = 0.871 \times 10^{100}$					
X ₁	4 59	3 62	3 60	+0 02	
X ₁	8 40	6 27	6 28	-0 01	
X ₁	14 23	10 19	10 24	-0 05	
Y ₁	14 65	10 41	10 52	-0 11	
X ₁	27 83	19 11	19 08	+0 03	
Y ₁	31 40	21 36	21 34	+0 04	
Y ₁	46 91	31 01	30 96	+0 05	
X ₁ Y ₁	Both fresh				

TABLE II -HEAT OF ADSORPTION MEASUREMENTS ON INACTIVE CHARCOAL

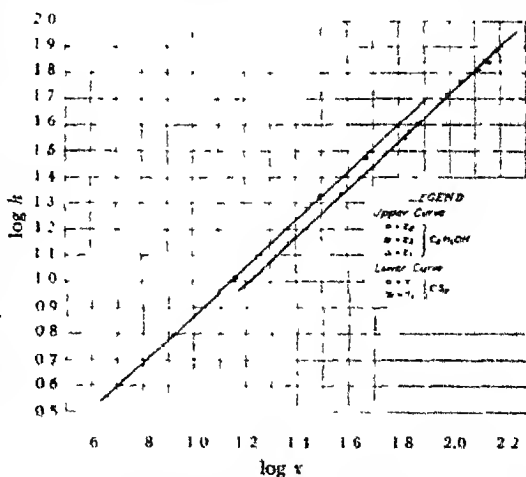
Carbon Tetrachloride					
$h = 0.841 \times 10^{100}$					
Charcoal and run	Adsorbed gas x cc	Heat evolved, h		Difference Δ cal	Pressure mm
		Observed cal	Computed cal		
V ₂	24 33	16 39	16 36	+0 03	
T ₂	26 12	17 45	17 48	-0 03	..
V ₂	36 27	22 5	23 73	(1 18)	21

TABLE II (continued).

Charcoal and run	Adsorbed gas x n cc	Heat evolved, h		Difference Δ cal	Pressure, mm
		Observed cal	Computed cal		
		Methyl Alcohol			
$h = 0.754 x^{0.928}$					
T ₁	32.65	19.95	19.84	+0.11	
T ₁	60.95	35.61	35.63	-0.03	2
T ₁	88.35	50.41	50.46	-0.05	4
T ₁	117.09	65.65	65.73	-0.08	14
Benzene					
$h = 0.824 x^{0.968}$					
V ₁	18.48	13.35	13.33	+0.02	
T ₂	23.71	16.74	16.94	-0.20	
V ₁	36.28	25.44	25.44	± 0.00	4
V ₁	47.93	33.16	33.16	± 0.00	9

In the first column of the tables there are letters indicating the charcoal samples used, together with the subscript indicating the number of the run. A₁, for instance, indicates that this measurement was made with charcoal A and is one of the experiments in the first run made with this sample. U₃ would mean the third run with charcoal sample U. The second column contains the quantities of gas (x) in normal cc. adsorbed

per g. of gas-free ad-
sorbent. In the third
column are given the
observed values of h ,
the heat evolved, in 15°
calories per g. of gas-free
charcoal. In the fourth
column are given the
values of h computed
from an empirical expo-
nential formula, placed
at the top of the column.
In the fifth column are
given the differences be-
tween the observed and
calculated values ($\Delta =$



$h_{\text{obs}} - h_{\text{calc}}$). The sixth column contains the equilibrium pressures observed at the time when the final calorimetric readings were made. The previous history of each charcoal sample is given below the results for each liquid.

If the observed values of x and h are plotted, they are found to lie on a system of lines slightly concave towards the x -axis. If the logarithms

of the values are plotted, they are found to lie very precisely upon straight lines, and this has been adopted as the most convenient way of representing our results graphically. (See Figs. 2, 3 and 4.) From the position and slope of these lines we obtain at once the constants of equations of the form

$$\log h = a + b \log x, \text{ or } h = mx^n$$

where $m = 10^a$ and $n = b$. The equations obtained in this way have been used to compute numerically the values of h given in the fourth column of the above tables.

Reproducibility and Reliability of Results.—The results presented above (Tables I and II and the curves) have been obtained with various weights of both active and inactive charcoal, some fresh, others previously used, and with various portions of gas, with reference to the weight of the charcoal. The agreement for each charcoal is very satisfactory. The average error of a single experiment seems to be about 0.7%, but that of the higher results is much less, due to compensation of errors in adding. The agreement between runs is about as good as that between experiments. This is shown particularly well by Fig. 2, where typical values obtained in 3 separate runs with ethyl alcohol and 2 separate runs with carbon disulfide are given. It is seen that the points lie very accurately on the same straight lines.

This close agreement shows that the total quantity of heat evolved during the adsorption by empty charcoal of a quantity of gas is definite and reproducible. It is not affected by the manner in which the gas is added (whether slowly or rapidly, all at once or in several portions) nor by the previous experiences of the charcoal, at least in our laboratory, provided that all the gas is first removed by heating to 350° and evacuating. In other words, it makes no difference whether the charcoal comes fresh from the can or has been previously used for other experiments, either with the same or a different gas; or, in the latter case, whether the gas has been immediately pumped out, or allowed to remain some time, or the charcoal even left open to the air. One interesting exception will be described later.

The reading of the calorimeter usually becomes constant after 15 minutes to a half an hour as stated above, and no slow creep of the calorimeter is noticeable; indeed, at least one of the runs (S_1) was begun and finished on different days. Had any appreciable heat been given off during the night the subsequent points, since each "experiment" was additive, would have been too low. No such effect was found. These facts demonstrate that if any slow sinking-in of gas occurred, no heat is thereby liberated. This is in agreement with the fact mentioned later, which our results have demonstrated in a striking fashion, that the

heat of adsorption is almost independent over a wide range of the amount of vapor already adsorbed. Any transfer, then, of adsorbed gas from the outer to the inner portions of the charcoal grain would liberate but a small and presumably inappreciable quantity of heat.

The measurements of the equilibrium adsorption pressure at the completion of an experiment do not have the same accuracy as the thermal measurements. Except in the case of carbon disulfide, however, these pressures must be very nearly correct, for no further noticeable change occurred after many hours. In the case of carbon disulfide there was a progressive decrease in pressure, so that in duplicate runs made at different

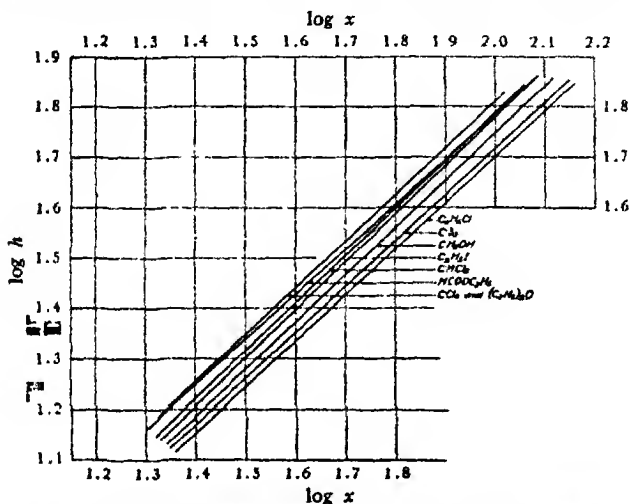


Fig. 3.—Variation of heats of adsorption with the amount adsorbed.

speeds the one made more rapidly, that is, with longer waits between the separate additions of the gas and hence with more opportunity for adsorption, gave higher pressures corresponding to the same amount of adsorption. In spite of this the heats evolved in the adsorption of the same amount of gas by the 2 charcoals differed by hardly more than the experimental error.

A very interesting effect occurs when carbon tetrachloride and other of the above-mentioned vapors containing halogen, except ethyl chloride, are used. Once having been used with these gases, a sample of charcoal cannot be brought back to its original condition, but appears to be changed in such a manner that in all subsequent experiments with it, less heat is evolved than would be by a new sample of the same weight. This is shown by the results tabulated in Table III.

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TABLE III.—EXPERIMENTS WITH POISONED CHARCOAL.

Carbon Tetrachloride.					
$h = 0.700 \times 10^{174}$.					
Charcoal and run.	Adsorbed gas cc.	Heat evolved, h.		Difference, Δ cal.	Pressure, mm.
		Observed cal.	Computed cal.		
D ₁	34.40	21 90	21 96	-0.06	..
A ₁	34.80	22.25	22 22	+0.03	..
A ₄	47.60	30.18	30 13	+0 05	..
A ₃	63.03	39.81	39 57	+0 24	..
A ₅	90 58	56 12	56 16	-0 24	20

A₃ Used first for CCl₄ and then for ether.

A₄ Same sample.

D₁ Used 5 times with CCl₄

Ether					
$h = 0.833 \times 10^{196}$					
K ₁	28 65	18 60	18 70	-0 10	.
A ₂	42 10	26 60	26 73	-0 13	..
K ₂	55 94	34 90	34 75	+0 15	..
A ₃	78.50	48 01	47 05	+0 36	12
K ₃	81 44	49 54	49 32	+0 22	10
K ₄	96.60	57 48	57 60	-0 12	80

A₃ Used with CCl₄

K₃ Used with CCl₄. Pumped in a vacuum overnight

Chloroform.					
$h = 0.716 \times 10^{180}$					
G ₁	30.20	18 47	18 84	-0 37	
F ₁	31.68	19.72	19 74	-0 02	
F ₂	65.01	39.42	39 38	+0 04	

F₂ Used previously with chloroform.

G₂ Ditto Stood 2 days under water, and exhausted one hour at 350°

Ethyl Bromide.					
$h = 0.543 \times 10^{102}$					
Y ₁	29.80	17 32	17 32		
U ₅	31 45	18.30	18 30		

Y₁ Used once with ethyl alcohol, and once with ethyl bromide

U₅ Used successively with benzene, twice with ethyl chloride, and with ethyl iodide. As the 2 results with the chloride were identical, it was considered that the poisoning was not due to that, but to the iodide.

It can be seen that the values obtained are perfectly consistent with themselves, whether made with carbon tetrachloride or ether, or chloroform. They run about 10% lower than with new charcoal, though the effect is a little less for the higher values. The capacity of the charcoal to adsorb gas is not noticeably affected. Subsequent experiments with carbon tetrachloride show no further effect on the charcoal, which continues to reproduce the results of the second run made.

The exact numerical relation can be seen from Table IV, where the

characteristic constants for the fresh and "poisoned" charcoal are collected.

TABLE IV.—COMPARISON OF FRESH AND POISONED CHARCOAL.

	m.		n.	
	Fresh.	Poisoned.	Fresh.	Poisoned.
CCl_4	0.893	0.700	0.930	0.974
$(\text{C}_2\text{H}_5)_2\text{O}$	0.917	0.838	0.9215	0.926
CHCl_3	0.8285	0.716	0.935	0.960
$\text{C}_2\text{H}_5\text{Br}$	0.900	0.543	0.900	1.02

It can be seen that except for ethyl bromide where only 2 measurements are available the n 's are substantially the same, while the m 's for poisoned charcoal are decidedly smaller.

These facts are shown even more clearly in Fig. 4, where the broken lines represent the behavior of the poisoned, and the unbroken lines that of the fresh charcoal. The 2 curves are almost exactly parallel, but the poisoned charcoal shows a constant lower heat evolution.

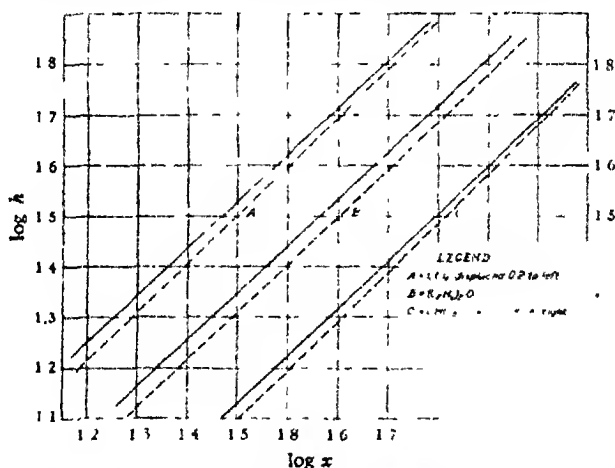


Fig. 4.—Poisoning effect of halogen-containing vapors. Solid lines represent fresh, broken lines "poisoned" charcoal.

The explanation of this behavior is not simple. That it is not due to incomplete removal of the carbon tetrachloride, is proved by the fact that in the second and subsequent runs just as much new gas is taken up (to a given pressure) as in the first; only the heat evolved is less. We, therefore, believe that the chloride reacts with some constituent of the charcoal, and that the reaction is completed during the first run or the subsequent exhaustion, after which no further change occurs. It seems unlikely that the change occurs *during* the first run, since the higher points determined ought to show the effect of it by running low. We thought

it might happen during the exhaustion preliminary to the second run, and tried varying the time and temperature of the exhaustion, but without influencing results. We did find, however, that if when a run is complete, the charcoal is removed from the calorimeter and allowed to stand at room temperature for an hour without removing any gas from it, and if the run is now resumed, the heat values will run somewhat low. If the charcoal is allowed to stand overnight, it will be found that the change has completely occurred, and the heats obtained from future experiments in the same run will correspond to those of second and later runs. This suggests that the change, whatever it may be, does not occur at all during the intervals of observation at the freezing point, occurs slowly at room temperature, and at any higher temperature occurs so rapidly that the change is completed even during the shortest period of exhaustion which we tried. Since prolonged exhaustion at high temperature does not cure this effect, it appears that there is no way of restoring a sample of charcoal which has once adsorbed carbon tetrachloride, except presumably by reactivation at a very high temperature, with air or another oxidizing agent.

Discussion of Results.—Since the above table and curves show clearly that the observed heats of adsorption on unpoisoned charcoal can be represented with satisfactory accuracy over the whole range as a simple exponential function of the amount of gas adsorbed, it is most convenient to discuss the results from the point of view of these equations, and the characteristic constants (m and n) which they contain. These constants have been collected in the first 2 columns of Table V.

TABLE V.—SUMMARY OF CALORIMETRIC RESULTS FOR ACTIVE CHARCOAL.

	n .	$(1-n)$	m .	h_m , cal.
C_2H_5Cl	0.915	0.085	0.7385	12.0
CS_2	0.9205	0.079	0.7525	12.5
CH_3OH	0.938	0.062	0.742	13.1
C_2H_5Br	0.900	0.100	0.900	13.9
C_2H_5I	0.956	0.044	0.737	14.0
$CHCl_3$	0.935	0.065	0.8285	14.5
$HCOOC_2H_5$	0.9075	0.092	0.944	14.5
C_4H_{10}	0.959	0.041	0.774	14.7
C_2H_5OH	0.928	0.072	0.871	15.0
CCl_4	0.930	0.070	0.893	15.3
$(C_2H_5)_2O$	0.9215	0.079	0.917	15.5

In the first place it is noteworthy that the exponents (n), are but slightly less than unity. This means that over the range studied the heat attending the adsorption of each successive equal increment decreases but slightly; in other words, that the system exhibits only slight fatigue. This becomes particularly evident if we express our equation in differential form,

$$\frac{dh}{dx} = \frac{mn}{x(1-n)}.$$

Evidently when $(1 - n) = 0$, dh/dx becomes a constant, that is, the heat evolved becomes independent of the amount already adsorbed. It can be seen that $(1 - n)$ is very small for these vapors.

How small these values are becomes particularly striking if we compare them with the corresponding constant for ammonia. The heats of adsorption of this gas on meerschaum have been measured over a fairly wide range at 0° by Chappuis,¹ and we have collected his results expressed in similar units to our own in Table VI. We have also computed an empirical equation of similar form to our own, and have included the values of (h) computed from this equation, in the table. It can be seen that there is an excellent correspondence between the observed and computed results.

TABLE VI.—HEAT OF ADSORPTION OF AMMONIA ON MEERSCHAUM.
According to Chappuis.
 $h = 2.23 x^{0.825}$.

Adsorbed gas x cc.	Heat evolved, h		Difference Δ cal	Pressure. mm.
	Observed cal	Calculated cal		
24.2	20.5	20.5	0	0
48.3	33.2	33.2	0	0.5
72.3	44.5	44.0	-0.5	3.71
95.3	53.47	53.4	+0.1	21.5
117.0	61.07	61.5	-0.4	57.56

The value of $1 - n$ for ammonia, 0.305, is 3 or 4 times as great as is the case for the vapors we have studied. The heat of adsorption of ammonia evidently changes rapidly with the amount of adsorption.

There is a decided parallelism between the exponents, n , and the boiling points of the above liquids. This is brought out in Fig. 5, where values of these constants for all the liquids studied are graphically represented. This parallelism means that the higher the boiling point of a liquid, the less marked the "fatigue." This relationship is confirmed by the large value of $1 - n$ for ammonia above mentioned.

The factors m (Table V), give an approximate measure of the heat effect for each gas, as the exponent n is so nearly unity and relatively so constant. It varies more widely than n ; namely from 0.737 for ethyl iodide to 0.944 for ethyl formate. There is a noticeable tendency for m to be large when n is small. This is particularly apparent when the value for ammonia is considered.

To obtain an exact measure of the heat effect of a given gas, we may compute the value for h of some particular value of x . Selecting $x = 44.6$, which is about the middle of our range, and which corresponds to

¹ Chappuis, *Ann. Physik.*, 19, 21 (1883).

one mol of gas per 500 g. of charcoal, and multiplying by 500, we obtain the values in the fifth column of Table V, which are the molecular heats of adsorption on 500 g. of this charcoal expressed in 15° kilogram calories.

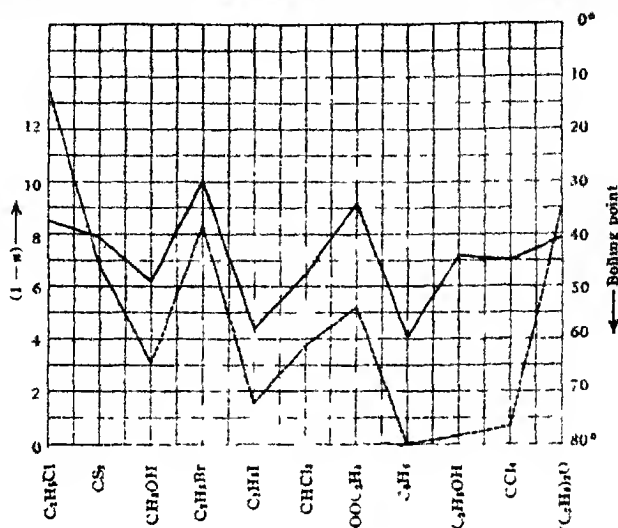


Fig 5—Relation between $(1-n)$ and the boiling point
Solid line = $(1-n)$, broken line = boiling point

The relatively small variation in the molecular heats of adsorption is noteworthy and would indicate some sort of compensating effect between the various factors on which the heat of adsorption depends

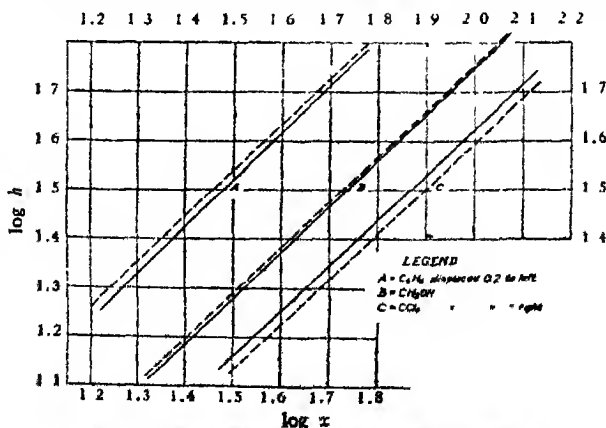


Fig. 6—Comparison of active and inactive charcoal.

The behavior of the inactive as compared with the active charcoal can be seen from examination of curves in Fig. 6 and the results collected in Table VII.

TABLE VII—COMPARISON OF ACTIVE AND INACTIVE CHARCOAL.

	<i>m</i>		<i>n</i>	
	Active	Inactive	Active	Inactive
CCl ₄	0.893	0.841	0.930	0.930
CH ₃ OH	0.742	0.754	0.938	0.938
C ₆ H ₆	0.774	0.824	0.959	0.955

It can be seen that so far as *n* is concerned there is scarcely any difference between the 2 charcoals; *m* is slightly smaller for carbon tetrachloride and somewhat larger for methyl alcohol and benzene. It will be noted that with benzene and carbon tetrachloride the pressure is much higher for the same amount of adsorption on the inactive charcoal, indicating a considerably lesser adsorptive power. With methyl alcohol there is little difference in this respect between the 2 charcoals.

All told, the heat values for the inactive charcoal agree quite closely with those of the active charcoal, particularly as regards the "fatigue" term.

The Net Heat of Adsorption.

The process of the adsorption of a gas can be pictured as taking place in 2 steps; first, the compression of the gas to such a point that liquefaction ensues, and second a further compression of this liquid by the adhesive forces of the adsorbent. The observed heat of adsorption will then be made up of 2 quantities, the latent heat of vaporization of the liquid, and what may be called the *net heat of adsorption*.

This is evidently nearly the same as the heat of wetting—and is precisely identical with it at the saturation pressure of the liquid. Since the latent heats of vaporization of these liquids are either known directly or can be calculated with accuracy from their known vapor pressure curves, the net heats of adsorption can readily be calculated from the observed heats of adsorption. The results thus obtained are given in Table VIII; the numbers in Col. 2 representing the molecular heats of adsorption when one cc. of the liquid is adsorbed per 10 g. of charcoal, those in Col. 3 the molecular heats of vaporization, and those in Col. 4 the net heats of adsorption under the same conditions.

It is evident from these figures that in general the net heats of adsorption are approximately of the same magnitude as the latent heats of vaporization. They vary from a third as much in the case of methyl alcohol to a third more in the case of ethyl ether.

With these facts before us we can now understand the regularity above-mentioned connecting *1* — *n* and the boiling points. Since the latent heats will, of course, exhibit no "fatigue," the greater the latent heats,

other things being equal, the less the fatigue. Since the net heats of adsorption do not as a matter of fact show any regular variation with the boiling points, and since high boiling liquids have high latent heats, these should in general show less fatigue and will, therefore, give smaller values of $1 - \eta$, as was found¹ to be the case.

TABLE VIII.—RELATION BETWEEN HEATS OF ADSORPTION AND HEATS OF COMPRESSION.

Column 1.	2.	3.	4.	5	6	7	8.	9
Gas	h , K. cal.	Q , K. cal.	$h-Q$, K. cal.	$(h-Q)$ 1 cc. K. cal.	$(\frac{dQ}{dP})$ 1 cc. cal.	$\frac{\text{Col. 5}}{\text{Col. 6}}$ 1000 at.	$(\frac{dQ}{dP})$ 1 cc. cal.	$\frac{\text{Col. 5}}{\text{Col. 8}}$ 1000 at.
C_2H_5Cl . . .	12 33	6.22*	6.11	0.0864	0.0101	8 5	0.00314	27 3
CS_2	12 63	6.83	5 80	0.0991	0.0073	13 5	0.00326	30 2
CH_3OH	12.95	9.33	3 62	0.0908	0.0076	12 0	0.00312	28 9
C_2H_5Br	14 33	6 85*	7 48	0.1020	0.0086	11 9	0.00349	29 2
C_2H_5I	14 25	7 81*	6 44	0.0815	0.0074	11.0	0.00312	26 1
$CHCl_3$	14 93	8 00	6 93	0.0875	0.0071	12 3
$HCOOC_2H_5$. .	15.42	8 38	7 04	0.0901	0.0087	10 3
C_6H_6	15 17	7.81	7 36	0.0850	0.0074	11 5
C_2H_5OH	14 98	10 65	4 33	0.0768	0.0066	11 6	0.00269	28.2
CCl_4	16 09	8 00	8 09	0.0856	0.0076	11 3
$(C_2H_5)_2O$. . .	16 09	6 90	9.19	0.0803	0.0097	8 3	0.00298	26 9
Average				0.0877		11 1		28 1
Mean deviation				+7 4%		±10%		±4%

* Computed from vapor pressure data.

Another interesting regularity appears when the net heats of adsorption per cc. of liquid are compared. These values, obtained by dividing the net molecular heat of adsorption by the molecular volume of the liquid at 0°, are given in Col. 5 of Table VIII. It can be seen that they are all very nearly identical, the average deviation from the mean (0.0877) being but 7.4%.

Additional evidence on this point can be obtained from the measurements of the heat of adsorption of ammonia and carbon dioxide on charcoal at zero degrees made by Titoff.¹ Plotting his somewhat irregular results for the heat evolved per cc. as a function of the volume adsorbed and taking data for the densities and latent heats at this temperature from the Landolt-Börnstein Tabellen, the values given in the second column of Table VIIIa, for the heat of adsorption per cc. of liquid on 10 g. of charcoal are obtained.

TABLE VIIIa.

	h , per cc. kg. cal.	Q , kg. cal.	$(h-Q)$ 1 cc. kg. cal.
CO_2	0.138	0.052	0.086
NH_3	0.293	0.187	0.103

¹ Z. physik. Chem., 74, 641 (1910).

It can be seen that the values of the net heats of adsorption per cc. (Col. 4, Table VIIIa), agree very closely with the average value which we obtained (0.0877).

This is a very illuminating fact. It indicates that the heat of adsorption is indeed due to the attractive forces of the charcoal upon the liquid, and that for a given volume of liquid, that is for a given volume of filled capillary space, the heat liberated is identical or nearly so for all the liquids studied.

If this net heat of adsorption does result from the forces of attraction acting on the liquid, it should be possible to compute from the known heats of compression how great this attractive force must be. The heats of compression of the liquids studied, in small calories per atmosphere per cc. of liquid at atmospheric pressure, have been calculated from the thermal dilatation at 0° by the well-known relation

$$dQ = \left(\frac{dv}{dT} \right) \frac{T}{42.7}.$$

The thermal dilatations here used were obtained by differentiating the series formulas given in the Landolt-Börnstein Tabellen, or in the more recent "Tables Annuelles." The results are given in Table VIII, Col. 6. With one or two exceptions they parallel quite closely the net heats of adsorption.

The quotients of the net heats of adsorption divided by the heats of compression should evidently represent the attractive forces acting on the respective liquids. These quotients are given in Col. 7, Table VIII. It can be seen that they are very nearly constant and of the order of 11,000 atmospheres. This high pressure, however, indicates at once that we are not justified in using heats of compression at one atmosphere pressure in making the computation. Instead we should use the mean heats of compression obtained by integration over the whole pressure range covered. Fortunately the heats of compression of 7 of the liquids we have studied have been computed by Bridgman¹ at pressures up to 12,000 atmospheres, based on his measurements of their compressibilities. Unfortunately, his pressure measurements were made only at 20°, 40°, 60° and 80°; but by plotting his values for the total heat of compression at 12,000 atmospheres against the temperature, smooth curves are obtained which permit a fairly accurate extrapolation to 0°. These extrapolated values of the heats of compression up to 12,000 atmospheres, expressed in small calories per atmosphere per cc. are given in Col. 8. Dividing now the net heats of adsorption by these more rigorous values, the attractive forces listed in Col. 9 are obtained. It can be seen that they show an even greater constancy and this indicates that the compressive

¹ *Proc. Am. Acad.*, 49, 1 (1913).

force exerted by the charcoal on all of these 7 very different liquids is identical within the experimental error.

This computed absolute value of the attractive force is still somewhat too small, for in general the mean heat of compression per atmosphere will

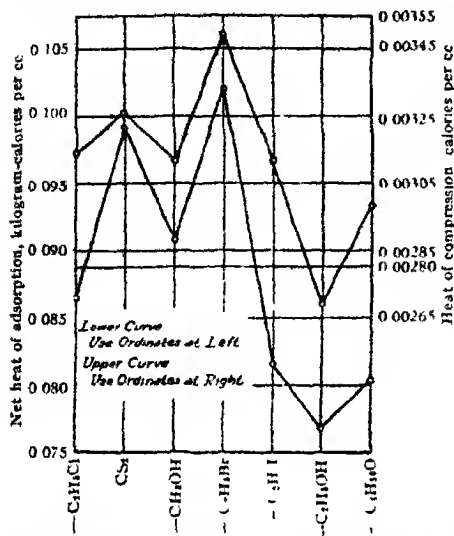


Fig 7 — Parallelism between wet heat of adsorption and heat of compression

that the net heat of adsorption is merely a heat of compression.

Adsorbability and Molecular Volumes. — Another very interesting regularity is disclosed when one compares the adsorbability of the liquids with their molecular volumes in the liquid state. For this purpose the adsorption pressures of all the liquids that have been studied have been plotted in Fig 8, where the pressure is represented as a function of the volume of gas adsorbed. Evidently, the volume of gas adsorbed at a particular pressure, say, 20 mm, would be a measure of the relative adsorbability of the gases. We have represented these values plotted against molecular volumes, in Fig 9, from which it can be seen that there is marked inverse proportionality between them. In other words, for this class of liquids, the greater the molecular volume of a liquid the less will be adsorbed at any given gaseous pressure.

The same regularity appears if we compare the adsorbabilities of ammonia and carbon dioxide as measured by Titoff¹ with their molecular volumes. At 20 mm pressure and zero degrees his charcoal adsorbed about 14 cc. of carbon dioxide and 24 cc. of ammonia, while the molec-

¹ *Z. physik. Chem.*, 74, 641 (1910)

be somewhat smaller at 28,000 atmospheres than at 12,000 atmospheres. As nearly as can be estimated from Bridgman's curves a further correction from 12,000 to 28,000 would lead to an average heat of compression of about 0.0024, and, therefore, to an attractive force of approximately 37,000 atmospheres. The relative values of the attractive force will be but slightly altered by this further refinement.

The parallelism of heats of adsorption and of compression are even better seen by Fig. 7, where these quantities are represented diagrammatically on the same scale. This evidence leaves but little doubt

ular volumes of these gases are respectively 48 and 26.8 cc. in the liquid state at this temperature.

Compared with the adsorbed volumes of the gases which we studied these volumes of carbon dioxide and ammonia are much smaller than

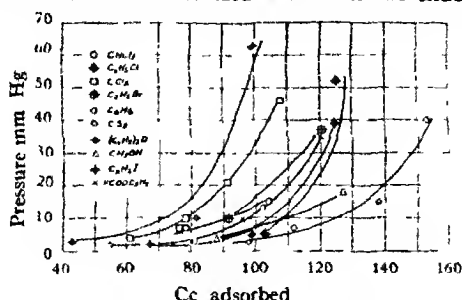


Fig. 8—Adsorption pressures at 0°.

All the pressure measurements made are included in this figure except those for the very rapid run with carbon disulfide and one irregular result for methyl alcohol, which is shown to be very much too large by similar measurements made on a less active charcoal. It should also be noted that the curve for ethyl ether has been drawn too far to the left. It should have passed near to the observed point at the coordinates 10 and 80.

would be expected, and indicate that this relation does not hold over so wide a range. However, Titoff's charcoal was certainly less active than ours, and the lesser volumes adsorbed may well have been due to this fact.

Adsorbability and Net Heat of Adsorption.—A final and at first sight still more surprising regularity appears when we compare the adsorbabilities of these liquids with the net heats of adsorption. Here again a reverse relationship is disclosed; the more adsorbable gas as measured by cc. of gas or number of mols adsorbed at a given pressure has the lesser heat of adsorption. This regularity is also shown graphically in Fig. 9. This relation appears at first almost paradoxical, but on further consideration it can be seen to follow neces

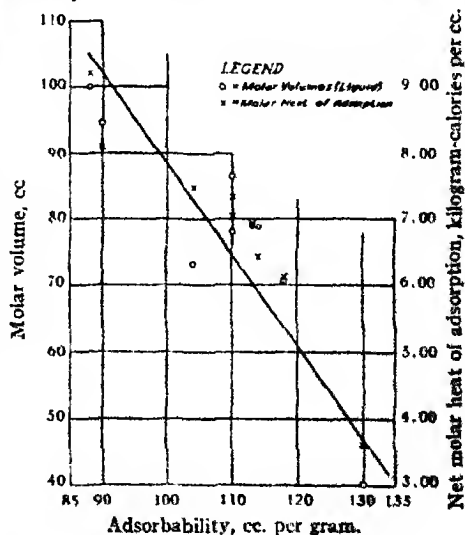


Fig. 9.

fully from the previous relationships that have been disclosed, and indeed serves as a striking confirmation of them. Thus, since one cc. of all these liquids evolves practically the same net heat of adsorption, the net heats of adsorption per mol are directly proportional to the molecular volumes of the liquids. But since the molal adsorbabilities are inversely proportional to the molecular volumes, it follows that the adsorbabilities are inversely proportional to the net molal heats of adsorption. Thus, for instance, since one volume of ether when adsorbed contains only half as many mols as does one volume of carbon disulfide, and develops the same net heat of adsorption, then the heat of adsorption of ether, mol for mol, will be twice as great as that of carbon disulfide. On the other hand, since ether has the larger molecular volume its adsorbability will be *less* that of carbon disulfide.

Nature of the Liquid Film.—The above-mentioned observation that the heats of adsorption vary so slightly with the amount adsorbed over the whole range, and the fact that the net heats of adsorption follow so closely the heats of compression characteristic of the various liquids *en masse*, both indicate that the adsorbed liquids are present in films many molecules deep. A similar conclusion is reached from a consideration of the actual weight and volume of liquid adsorbed as compared with the probable area of the capillary surface. Thus, the largest amount of gas whose heat of adsorption was measured was in the case of carbon disulfide, of which 153 cc. was adsorbed on one g. of charcoal. This corresponds to 0.4 cc. of liquid carbon disulfide at atmospheric pressure and to about 0.25 cc. under a pressure of 37,000 atmospheres. Even with this amount of gas adsorbed the saturation pressure of liquid carbon disulfide was not reached. Hulett¹ has found that this active charcoal with a "block" density of about 1.07 has a capillary volume of about 0.42 cc. Evidently the carbon disulfide filled most of the capillary space. Hulett² has estimated that the capillary area of this active charcoal is no greater than 200 square meters per gram. Taking it as 100 square meters and assuming that the thickness of a molecular layer is 1×10^{-8} cm., then the above amount of carbon disulfide if spread over the whole surface would have given a layer 40 molecules deep. The smallest volume on which observations were made was in the case of ethyl alcohol, where the heat of adsorption of 3.62 cc. was measured. This corresponds to a volume of 0.01 cc. of liquid alcohol or to a layer about one molecule thick.

Finally, in support of this point of view there is the evidence presented by Quincke³ that the molecular sphere of action of silver has a radius of 6×10^{-8} cm. and would, therefore, extend far beyond the thickest films above mentioned.

¹ *This Journal*, 42, 391 (1920).

² *Loc. cit.*

³ *Pogg. Ann.*, 137, 402 (1869).

The only fact that apparently conflicts with the above interpretation is the greatly reduced vapor pressure exhibited by the liquid adsorbed upon the charcoal surfaces. If this liquid is under as great a pressure as we have computed, one might at first glance expect its vapor pressure to be considerably increased. But this pressure is not an unbalanced one; it is not applied solely to the liquid phase, but exerts its effect upon the escaping gaseous molecules as well. As a result it can have no tendency to increase the vapor pressure of the liquid phase, and indeed its net effect must be to lessen the vapor pressure of the liquid film, at least until this film extends beyond the limit of its sphere of action.

Summary.

1. Measurements of the heat of adsorption of the vapors of some 11 organic liquids upon charcoal at 0° have been made over a considerable range. The resulting values have been shown to be reproducible and independent of the rate of the adsorption of the vapor and of the previous history of the charcoal.

2. The heats of adsorption of all of these vapors can be represented very precisely as functions of the amount adsorbed by the expression $h = mx^n$, where h represents the heat of adsorption per normal cc. of vapor, x the number of cc. of vapor adsorbed, and m and n constants characteristic of each vapor.

3. The constant n in the above equation has been found to be very nearly unity. The heat of adsorption, therefore, decreases but slightly with increasing amount of adsorption. In other words, there is but slight evidence of "fatigue" in the adsorptive forces.

4. It has been shown that this decrease (represented by $1 - n$) is antipathetic to the boiling points of the liquids; that is, the liquids with relatively high boiling points exhibit a small value of $1 - n$ and hence a slight fatigue. This is due to the fact that such liquids have high latent heats of vaporization.

5. m also varies relatively little from vapor to vapor. In general m and n tend to vary in opposite directions. In agreement with this the actual molal heats of adsorption of the various liquids measured are not very different, varying between 12.0 cal. for ethyl chloride and 15.5 cal. for carbon tetrachloride.

6. The heats of adsorption of these vapors are very nearly the same on inactive as on active charcoal of the same kind.

7. Vapors containing halogens appear to react with the charcoal when warmed, so as to decrease the heat evolved by any subsequent adsorption of gas, without, however, affecting greatly the fatigue effect.

8. The net heats of adsorption, that is the heats evolved above those corresponding to the latent heats of vaporization, are approximately of the same magnitude as the latent heats of vaporization.

9. The net heats of adsorption per cc. of liquid are very nearly identical for all the liquids studied.

10. The net heats of adsorption are closely proportional to the heats of compression under high pressure. This indicates that the liquids are all attracted by the charcoal with substantially the same force—and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres where 1 cc. of liquid is adsorbed on 10 g. of charcoal.

11. The molar adsorbability, that is the number of cc. of gas adsorbed at a fixed gaseous pressure (20 mm.), is inversely proportional to the molecular volume of the liquid.

12. The molar adsorbability is inversely proportional to the net molar heat of adsorption. This, at first sight, surprising behavior is shown to follow necessarily from the previously mentioned regularities.

13. It is shown that all the above evidence indicates that the liquid films we have studied are all at least one and usually very many molecules thick, and this is confirmed by a consideration of the actual volume occupied by the liquid and the approximately known capillary volume and surface of the charcoal.

WASHINGTON, D C

NEW DETERMINATION OF THE ABSOLUTE VALUE OF THE RADIUM : URANIUM RATIO.¹

BY S C LIND AND L. D. ROBERTS

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1. Historical.

The value of the radium : uranium ratio, first determined by Rutherford and Boltwood² in uraninite from North Carolina, was originally reported as 7.4×10^{-7} . The following year it was found³ that a serious error had been made in the value of the radium standard solution, caused by partial precipitation of the radium. Accordingly, the value of the ratio was changed to 3.8×10^{-7} . A little later, Boltwood⁴ redetermined the uranium content of the standard uraninite, which lowered the value still further to 3.4×10^{-7} . This remained the accepted value for several years.

After the International radium standard was adopted in 1910, Rutherford⁵ made a comparison with his previously used radium standard,

¹ Published with the permission of the Director of the U. S. Bureau of Mines under the cooperative agreement with the Colorado School of Mines.

² Rutherford and Boltwood, *Am. J. Sci.*, [4] 20, 55-6 (1905).

³ Rutherford and Boltwood, *ibid.*, 22, 1 (1906).

⁴ Boltwood, *ibid.*, [4] 25, 296 (1908).

⁵ Rutherford, *Phil. Mag.*, [6] 28, 320-7 (1914).

which indicated a change from 3.4 to 3.23×10^{-7} for the radium: uranium ratio.

In 1913 Heimann and Marckwald¹ examined 8 specimens of pitchblende from the principal uranium deposits of the world and found the ratio to be constant within 0.4% and reported the absolute value as 3.328×10^{-7} . Their radium solution was made from 4.85 mg. of radium chloride of 30% purity, obtained from the Institut f. Radiumforschung in Vienna.

In 1915 Becker and Jannasch² determined the ratio in selected Austrian pitchblende which was analyzed with great care, not only for uranium, but for all the other elements present. Their standard radium solutions were prepared from 2 portions of radium chloride containing 2.144 and 2.249 mg. of radium element, respectively, which were also obtained from the Radium Institute in Vienna. The solutions were prepared with due regard for the protection of radium in solution by the addition of barium and of hydrochloric acid. The values reported by Becker and Jannasch were " $3.383 \times 10^{-7} \pm 1.0\%$ for the solution method, and $3.415 \times 10^{-7} \pm 0.7\%$ for the fusion method" of treating the pitchblende.

Between the corrected Rutherford value (3.23×10^{-7}) and that of Becker and Jannasch, there is a discrepancy of about 5.5%, and about 2% between the value of Heimann and Marckwald and that of Becker and Jannasch. It, therefore, appeared very desirable to redetermine this important constant which has not only great theoretical but also much practical interest, since pitchblende is very commonly used in standardizing emanation electroscopes for the determination of radium by the emanation method.

For example, if the radium determinations for plant control in the production of radium were being carried on by means of electroscopes standardized with analyzed pitchblende, the value of the radium: uranium ratio would have a direct influence on the accuracy of the results. If all the measurements were based on this ratio, they might all be relatively correct among themselves, but absolutely in error by the amount of error in the ratio. Usually, however, radium is withdrawn from the crystallizing system and measured by the γ -ray method, which is independent of the radium: uranium ratio since it depends solely on the International standard. It will, therefore, be seen that if the radium were being measured into such a system by means of the ratio and taken out by the γ -ray measurement, an accumulative discrepancy would be produced between the real and the apparent radium content of the crystallizing system, which in time would become a very large one.

¹ Heimann and Marckwald, *Jahrb. Radioakt. Elektronik.*, 10, 299-323 (1913).

² Becker and Jannasch, *ibid.*, 12, 1-34 (1915).

2. Sources of Error.

Briefly, the sources of error may be summarized as follows.

1. As regards the radium standard solution, accurate results could not be obtained until the careful atomic weight work of Hoenigschmid and Mme. Curie had opened the way to the establishment of a correct radium standard. Even then, the small quantities of radium that had usually been available for determining the ratio have rendered an exact knowledge of the radium content of the standard solutions fairly doubtful. A γ -ray measurement of rather small quantities of radium sometimes had to be followed by the weighing out of still smaller quantities of radium salt, which is rather hygroscopic.

2. As regards the radium solution prepared from the standard salt, there arises the difficulty of maintaining all the radium in solution. This was extremely difficult before the protective action of an excess of barium and acid was thoroughly understood. If partial precipitation occurs, the solution does not yield its full quantity of emanation. It has now been demonstrated¹ that radium is retained in a properly protected solution. With respect to pitchblende, the difficulty of keeping radium in solution is enhanced by the sulfur impurities in the ore. This disadvantage is encountered only when the pitchblende is dissolved and stored for the accumulation of emanation.

3. The difficulty of the correct analytical determination of uranium is not inconsiderable, as has been clearly shown by Becker and Jannasch.²

4. The difficulties of the electroscopic determination of radium emanation have also to be contended with. Owing to the nature of the instrument, a rather large number of repetitions of each determination is necessary to insure any degree of precision.

3. Experimental Procedure.

A. Preparation of a Radium Standard Solution.—One of the portions of radium salt prepared from Colorado carnotite by the U. S. Bureau of Mines³ consisted of a tube of anhydrous radium chloride of a total salt content of 0.2067 g. Comparison by the γ -ray method with the International standard of the U. S. Bureau of Standards showed a content of radium element of 157.3 mg. Since the salt was believed to be 100% RaCl_2 , the radium content could also be calculated directly from its known weight, using Hoenigschmid's value (226.0)⁴ for the atomic weight of radium. This calculation also gives 157.3 mg. of radium, thus affording an independent check of the radium content, and giving great reliability to the value.

¹ J. Moran, *Trans. Roy. Soc. (Canada)*, 10^{III}, 77-84 (1916).

² *Loc. cit.*

³ *Bur. Mines, Bull.* 104.

⁴ O. Hoenigschmid, *Sitzb. Akad. Wiss., Wien*, 120, Abt. IIa, 1617-52 (1911).

The tube was opened, and the salt content dissolved in 5% redistilled, sulfate-free hydrochloric acid solution. The salt went completely into solution without any trace of cloudiness.¹ The tube was carefully washed several times with more of the 5% acid and the solution was finally diluted to one liter of acid of the same strength and thoroughly mixed.

From this solution 10 cc containing 1.573 mg of radium element was immediately pipetted into 5% HCl and made up to one liter, to which was added about 23 mg of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. From this solution, after thorough mixing, 10 cc containing $1.573 \times 10^{-4} \text{ g}$ of radium was immediately pipetted into a solution which was made up to one liter with 5% HCl and to which 2 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ were added. From this solution, after thorough mixing, 100 cc containing $1.573 \times 10^{-4} \text{ g}$ of radium was at once pipetted into a solution which was made up to one liter of 5% HCl and 2 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. This solution, when thoroughly mixed, constituted the final standard solution, in which the radium was protected by one million fold of barium and 5% HCl.

From this standard solution, 12 portions of 10 cc. each, containing $1.573 \times 10^{-4} \text{ g}$. of radium, were at once pipetted into 1 : 1 nitric acid solution, half filling twelve 125 cc. Pyrex flasks. Four different pipets and 4 different measuring flasks were calibrated for use in the dilutions just described, no vessel was used for more than one concentration of solution. By having all preparations previously made, only 1.5 hours were consumed from the time the radium tube was opened until the 12 solutions were sealed up in 1 : 1 nitric acid for the accumulation of radium emanation, thus avoiding the possibility of precipitating radium sulfate by slowly dissolving sulfate from the glass vessels.

Before the accumulation of emanation, the solutions were boiled 15 minutes in Pyrex flasks to reduce the emanation to zero, and were then sealed by drawing out the neck of the Pyrex flask in an oxygen-gas flame so that a connection could be later made with rubber tubing, enabling the breaking of the glass tips under the rubber connection. This practice precluded the possibility of loss of emanation by leakage. By this procedure, it is believed that all errors, mentioned under Sections 1 and 2 above, were practically eliminated. The emanation was allowed to accumulate for various periods from 5 to 10 days before boiling off for the electroscopic determination.

B. Analysis of Pitchblende.—The standard pitchblende used was selected Colorado pitchblende, as homogenous and free from sulfur as possible. The sulfur content was not determined, since the method employed of directly dissolving the pitchblende, instead of storing the solution, renders the presence of sulfur far less objectionable than when the pitchblende is allowed to stand in solution for the accumulation of radium emanation. The pitchblende was ground to pass 200 mesh. Its

¹ Since this portion of radium chloride had been prepared about 2 years previous to its opening, it was interesting to note that 100% RaCl_2 is not rendered insoluble in acid by its own radiations.

emanating power was determined by the Boltwood method¹ of storing for one month in a closed tube and then drawing air slowly over it into the electroscope chamber. The emanating power, or per cent., of emanation spontaneously diffusing from the ground sample, was found to be 5.65% of the total possible.

The uranium content was determined by the Ledoux method, which has been in use for several years at the U. S. Bureau of Mines, and has been described as applied to carnotites by Lind and Whittemore.² Such parts of the procedure as referred to the separation of vanadium were omitted in the case of pitchblende. The gravimetric determination of the U_3O_8 from 1 g. of pitchblende gave a value of 0.7796 g., which, using the Hoenigschmid value³ for the atomic weight of uranium (238.2), is equivalent to 0.6612 g. of uranium per gram of pitchblende.

C. Treatment of Pitchblende for the Radium Determination.—40 to 50 milligrams was carefully weighed on an assay balance and removed from the pan into a small (7 cm.) quantitative filter paper. The pan was cleansed with a small piece of the same paper which was included in the determination. The determination was then carried out as described by Lind.⁴ Twenty determinations of the emanation content were carried out in 3 different emanation chambers with 2 different electroscope heads (see Section E), in order to obtain a precise average result.

D. Treatment of the Radium Standard Solutions.—After the 12 solutions had accumulated emanation for periods of 5 to 10 days, they were connected to the emanation collecting apparatus just as in the case of pitchblende. After breaking the tips under rubber connection, the solutions were boiled off in the same manner. The gas was then transferred into the electroscope emanation chamber, where it was allowed to stand until equilibrium was attained with induced activity.

E. The Electroscopic Measurements.—The "interchangeable head" type of electroscope employed by the Bureau of Mines was used.⁵ Three chambers and two interchangeable heads were used; each combination being standardized by at least 3 determinations, both with pitchblende and with a radium standard solution. The latest types of the instruments were employed.⁶

The only further precaution concerns the pressure and temperature of the air in the electroscope chamber at the time of measurement. After introducing the emanation into the chamber, a slight vacuum was left during the 3-hour period of accumulating induced activity. This served

¹ B. B. Boltwood, *Phil. Mag.*, 9, 599 (1905).

² *This Journal*, 36, 2076 (1914).

³ O. Hoenigschmid, *Z. Elektrochem.*, 20, 452 (1914).

⁴ S. C. Lind, *J. Ind. Eng. Chem.*, 7, 1024 (1915).

⁵ S. C. Lind, *Ibid.*, 7, 406 (1915); modified form, *ibid.*, 12, 469 (1920).

⁶ *Loc. cit.*

the double purpose of avoiding the possibility of any outward leak, and also of permitting some regulation of the external room temperature at the time of final equalization of pressure to the prevailing barometric pressure. At this elevation the average of pressure is about 620 mm. Therefore, 620 mm. and 20° were chosen as normal conditions. Any departure of the barometric pressure from 620 was compensated as far as possible by a corresponding regulation of room temperature so as to avoid correction. The nature of the correction for electroscopes of one-half liter gas capacity can hardly be linear, but, apparently from comparison of results of O. C. Lester¹ for larger chambers and lower pressures, would not be far from direct proportionality; so that such small corrections as have been applied (average 0.6%; maximum 1.5%) were made linearly, doubtless improving the results even though some slight over-compensation may have resulted.

The natural leaks which were subtracted from the electrical discharge were the results of actual blanks carried out with all the reagents, except radium, just as in the determination. They exceeded the usual natural leaks of the instruments themselves by about two-fold; but even then constituted corrections on the rate of discharge of only 0.4 to 1.0%, which remained quite constant.

4. Experimental Results.

The 3 electroscopes chambers used were designated I, II and III; the 2 interchangeable heads, A and B. By reading each chamber with each head, 6 combinations were obtained: A_I, B_I, A_{II}, B_{II}, A_{III} and B_{III}. Standardization of each combination in terms of grams of radium $\times 10^{-8}$ for a discharge of $\frac{1 \text{ div.}}{1 \text{ sec.}}$ was established by 3 or 4 determinations each with

standard pitchblende and with the radium standard solution. The provisional ratio used for pitchblende was the Heimann and Marckwald value, 3.328×10^{-7} , correction for the emanating power of the pitchblende was, of course, applied. The results are shown in Table I.

The results indicate that the Heimann and Marckwald value (3.328×10^{-7}) is low by 2.1%. Multiplying it by the value, 1.021, gives as the final radium : uranium ratio of these determinations $3.40 \times 10^{-7} \pm 0.03$. This value is in splendid agreement with those of Becker and Jannasch ("3.383 $\pm 1\%$ and 3.415 $\pm 0.7\%$," average 3.399×10^{-7}), and indicates that the old Rutherford and Boltwood value, 3.4×10^{-7} is correct to within less than 1%.

It is assumed that the relative constancy of the radium : uranium ratio for different pitchblendes has already been thoroughly established by Heimann and Marckwald.² Lind and Whittemore³ have also shown that

¹ O. C. Lester, *Am J Sci*, 44, 225 (1917)

² *Loc. cit.*

the same ratio holds for carnotite when the sample represents sufficiently large quantities of the ore to compensate local concentration.

TABLE I.

Values Refer to Radium in g. $\times 10^{-3}$ for a Discharge of $\frac{1 \text{ div.}}{1 \text{ sec.}}$					
Electroscope.	Ra solution.	Average.	Pitch-blende.	Average.	Relative ratio.
	8.175		7.989	7.994	
A ₁	8.042	8.099	7.980		101.3
	8.081		8.013		
	7.536		7.300		
B ₁	7.649	7.600	7.357	7.329	103.7
	7.614		7.330		
	8.065		8.021		
A _{II}	8.104	8.112	8.030	8.053	100.7
	8.168		8.065		
			8.097		
	7.698		7.391		
B _{II}	7.501	7.609	7.326	7.336	103.7
	7.628		7.348		
			7.278		
	8.137		8.106		
A _{III}	8.254	8.228	8.179	8.125	101.3
	8.299		8.091		
	7.544		7.485		
B _{III}	7.637	7.591	7.432	7.442	102.0
	7.593		7.409		Final average 102.1 $\pm 1\%$

NOTE.—The question has recently been raised whether duplicate emanation chambers could be practically constructed so as to have identical calibration constants in order to avoid the necessity of calibrating more than one chamber. Some interesting light is thrown on this subject by comparing the results of Table I. The chambers were used as furnished by the makers; no especial efforts having been made to have them exactly identical. It will be seen that Chambers I and II have identical constants within the limits of experimental error, as indicated by the results for both heads A and B. Chamber III shows a small apparently real deviation. These results indicate that with a small amount of care on the part of the maker, chambers can be duplicated which will have identical constants for all ordinary purposes.

5. Summary.

1. A standard radium solution was prepared by dissolving in one liter of 5% redistilled hydrochloric acid, 0.2067 g. of 100% radium chloride containing 157.3 mg. of radium element, as shown both by calculation from the chemical formula and by the γ -ray comparison of the U. S. Bureau of Standards with the International radium standard. The clear solution was diluted with 5% hydrochloric acid until one liter contained 1.573×10^{-4} g. of radium, protected by one-million fold of barium chloride.

2. The standard radium solution was used to standardize by the Bureau

of Mines method 3 electroscopes chambers, each of which was measured with 2 interchangeable leaf chambers.

3. The same chambers and heads were standardized against U. S. Bureau of Mines standard pitchblende from Colorado.

4. The results give as final average of 18 determinations $3.40 \times 10^{-7} \pm 0.03$ for the ratio radium : uranium. The result agrees with the average of Becker and Jannasch, 3.399×10^{-7} obtained at the Radiological Institute at Heidelberg, using standard radium salt from the Institute of Radium Research in Vienna, and with the old uncorrected value 3.4×10^{-7} of Rutherford and Boltwood.

The writers express with pleasure their indebtedness to Messrs. J. P. Bonardi and J. E. Conley for their kindness in recrystallizing the 100% radium bromide from which the pure radium chloride was prepared, and also to Dr. N. E. Dorsey, of the U. S. Bureau of Standards, for making the γ -ray comparison with the International standard.

GOLDEN, COLORADO.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF
COMMERCE]

A WEIGHT BURET FOR GAS ANALYSIS.¹

BY E. R. WEAVER AND P. G. LEDIG

Received April 3 1920.

The use of a weighing method for making gas measurements was suggested by the great advantages of a weight buret for liquids over the older volumetric burets. The apparatus here described was designed primarily for use in a forthcoming study of gas-analysis methods; but it appears to have sufficient application, for any gas volumetric measurements requiring greater precision than is easily obtainable with an ordinary gas buret, to warrant publication at this time. A description of the apparatus and its method of use will first be given; then the reasons for various details of construction will be considered; the principal sources of error will be pointed out; and finally some typical experimental results which show the precision obtainable will be given.

Description and Method of Use.

For the sake of clearness, the apparatus is represented in Fig. 1, as though constructed in a single plane. Actually, the tubes and bulbs may be arranged in any convenient manner, if the relative levels of the different parts are kept approximately as shown. In the apparatus constructed all the parts which had to be water-jacketed, fitted neatly into a round battery jar of about twice the diameter of Bulb A.

By means of connections to vacuum and air pressure, which are sup-

¹ Published by permission of the Director of the Bureau of Standards.

operated by a small motor-driven pump, mercury may be drawn into or forced out of Bulbs B or D through Stopcocks *c* and *e*. When the apparatus is ready for use, Bulb A and Tubes 1, 3, 4 and 5 are completely filled with mercury, which also fills Tube 6 nearly up to the contact point *p'*. When, as is usually the case, the gas is to be measured saturated with water vapor, a drop of water is included in the compensator C, and a little water is allowed to wet the walls of the buret

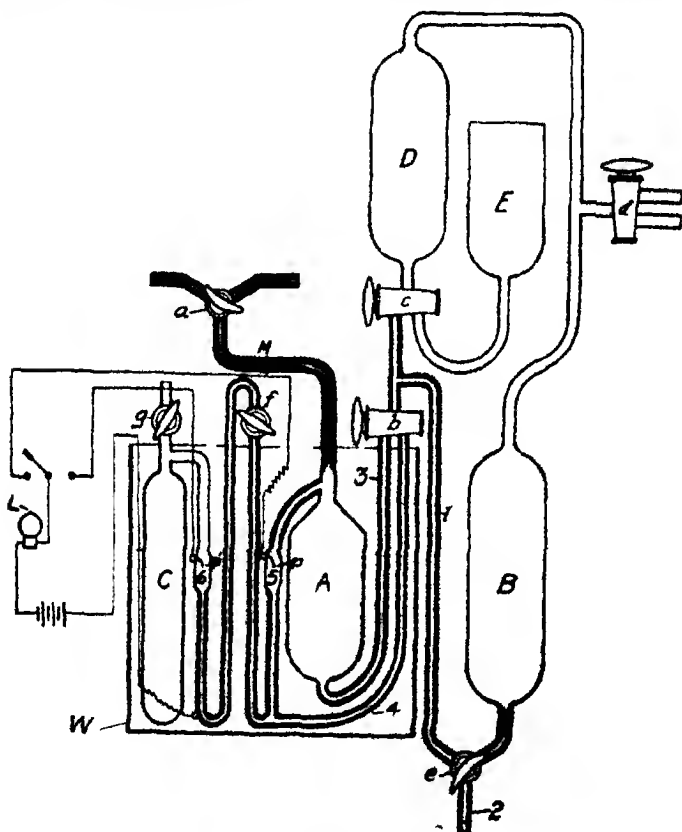


Fig. 1.

The method of making a gas measurement is as follows. With Stopcock *f* open, the level of the mercury in Tube 6 is carefully adjusted to exactly close the contact at *p'* by running in mercury from D. Stopcocks *f* and *g* are then closed, confining a fixed volume of gas in the compensator C. The measuring Bulb A is now connected through *a* with the vessel containing the gas to be measured and mercury is withdrawn into

D until the surface of separation of the gas and the confining liquid in the buret reaches the mark M. Stopcock *c* is now closed; Stopcock *e* is turned to connect A and B and the gas is drawn into A, the mercury displaced flowing into B. The surface of separation between the gas and the confining liquid following the gas is stopped just at mark M by closing Stopcock *a*. The volume of mercury in B is now exactly equal to the volume of gas in A; it remains to run mercury from B to A until the pressure of the gas in A is adjusted to equal that in the compensator C. Mercury is first drawn into B through Tube 4 until the contact point in 5 is uncovered; then it is forced back until the contact is just closed as shown by the electric light L. The amount of mercury in the compensator between points 5 and 6 is thus accurately adjusted. Stopcock *b* is closed to Tube 4 and opened to Tube 3, Stopcock *f* is also opened; and by running mercury between A and B through Tubes 1 and 3 the pressure in A is carefully adjusted, until the contact in 5 is again just closed, final adjustment always being made with a rising meniscus. Assuming that contact-points *p* and *p'* are on the same level, the pressure of the gas in A is now exactly equal to that in compensator C, and its volume is exactly equal to the volume of the mercury in B. Stopcock *e* is turned to connect B to Tube 2 and the mercury run into a small flask in which it is weighed. From the weight found, the volume of the mercury, equal to the volume of the gas in A, is easily determined.

The process of adjustment appears very tedious on paper, but really does not require much more time of an observer familiar with the apparatus than does the adjustment and reading of an ordinary buret using a Peterson compensator. Bulb D is merely a mercury reservoir into which mercury can be introduced at will through Funnel E. When the gas is to be transferred from A to an absorbing pipet or other container, Stopcock *f* is closed, Tube 5 is filled with mercury run from D through Tube 4 and finally the entire volume of gas in A is displaced with mercury introduced from D through Tube 3.

Merits of the Apparatus.

The apparatus has the following advantages.

1. The measurement of the actual volume of gas is very accurate, the probable error being ordinarily much less than the probable error in making the pressure adjustment. This measurement is independent of the condition of the meniscus, of whether water or other liquid is present on top of the mercury, of drainage, and of drops of liquid sticking to the walls of the measuring vessel.
2. Small volumes are measured directly and with great accuracy; a pressure correction is of course necessary when the volume is less than that of the tubes between Mark M and contact-point *p*.
3. The observer can form no idea what his results will be until he has

weighed the mercury. If a proper balance is used this final measurement is not subject to an appreciable observational error, consequently the observer is entirely unbiased by any notion of what the result should be.

4. The reading does not depend in any way upon the reading of a graduated scale and is, therefore, free from errors of calibration and errors due to parallax.

5. The apparatus is short and compact; the changes of mercury level, being small, are easily made by means of air-pressure adjustments; and the difficulty of reading a long vertical scale is eliminated.

6. The apparatus is easily jacketed in a jar of convenient size and shape. No connection goes through the jacket, which can be removed at once for cleaning or repairing the apparatus; this also eliminates any difficulty in making the jacket water-tight.

7. The apparatus, if properly constructed, can be completely drained of mercury and filled with a cleaning solution without disturbing any of the connections.

8. The gas to be measured is never in contact with a stopcock, rubber tube, or other possible source of leakage except while being transferred through Stopcock A, and it is easy to avoid excessive pressures either above or below atmospheric when making this transfer.

9. The gas is always completely expelled from the buret when it is transferred to a pipet or other container. This eliminates one of the principal disadvantages of the familiar Peterson compensator in which there is a considerable residual volume of gas which can be transferred only by tedious and careful manipulation, and at the risk of spoiling the compensation by running mercury from the compensator into the buret.

10. The surface of the mercury at p , can always be made fresh by forcing mercury into A through Tube 4, and that without transferring the gas sample or affecting the filling of the compensator. This is very important where an electrical contact is used in adjusting the compensator and would be of value even if the mercury in the compensator were adjusted to a line on the glass.

11. There are no rubber connections to foul the mercury or to give trouble in other ways.

12. The apparatus may be made of any desired capacity without loss of accuracy, and no facilities for graduating it are required as in the case of a special volumetric buret.

Details of Design.

In general, the dimensions and other details of construction of the apparatus are determined only by convenience and have little to do with the accuracy of the measurement. The platinum points p and p' must be on very nearly the same level, otherwise an error results in the compensation for changes of temperature, amounting to about one part

in 20,000 of the volume measured per degree change in temperature per millimeter difference in levels. Obviously it is not difficult to so adjust the levels of these points that this correction will be negligible under ordinary conditions.

Experiments which need not be described here were made to determine the relative accuracy and convenience of adjusting the mercury surface in the compensator to a line, adjusting to make visible contact with a glass or metal point, and adjusting to make electrical contact as proposed by Gregg.¹ It was found that the last mentioned method generally gave the greatest accuracy and was by far the most convenient. This method was, therefore, adopted, practically the only objection to it is the possibility of a little dirt such as a particle of stopcock grease, adhering to the platinum point and changing the height at which the mercury meniscus makes contact.

The approximate diameter of the enlarged portions of Tubes 5 and 6 required to give minimum error was also determined experimentally; the point is hardly of sufficient importance to justify a description of the several methods employed. It is sufficient to state that it was found that the minimum average error occurred with tubes having diameters from 8.5 to 13 mm., there being little difference over this range. The average error was much greater with tubes of much smaller diameter because of the tendency of the mercury to stick to the walls, tubes larger than 13 mm. gave increasing errors because of the effect of any error in adjusting the levels, upon the relative volumes of compensator and buret. A diameter of one cm. was chosen for these tubes and appears to be about right for a measuring vessel of not over 150 cc. capacity.

A large compensator-volume is, of course, favorable to accurate results because any error in adjusting mercury levels makes less relative difference in the volume of gas confined; but the advantage of making it larger than 25 cc. is not great. In order to accommodate all necessary parts within the jar selected for a water jacket, the compensator actually constructed has a volume of about 35 cc.

The apparatus for supplying positive and negative pressure is shown diagrammatically in Fig. 2, which is practically self-explanatory.

Sources of Error.

It is not proposed to thermostat the apparatus because, with the changes of temperature occurring in the ordinary use of the instrument, the errors in compensation due to temperature change are less than the accidental errors of pressure adjustment. With the apparatus as now constructed the following remaining sources of error may be mentioned.

1. Errors in setting the meniscus to the mark M on the inlet capillary. This error enters twice into every measurement.

¹ *J. Ind. Eng. Chem.*, 9, 528 (1917).

2. Errors due to incorrect adjustment of the mercury levels. Since there are 3 adjustments, there are 3 chances of making this class of errors. These errors are due to (1) sticking of the mercury to the walls of the tubes,—probably the most important source of error involved in the whole method of measurement; (2) failure of the mercury to make instant contact with the platinum point because of a film of dirt on mercury or platinum; (3)

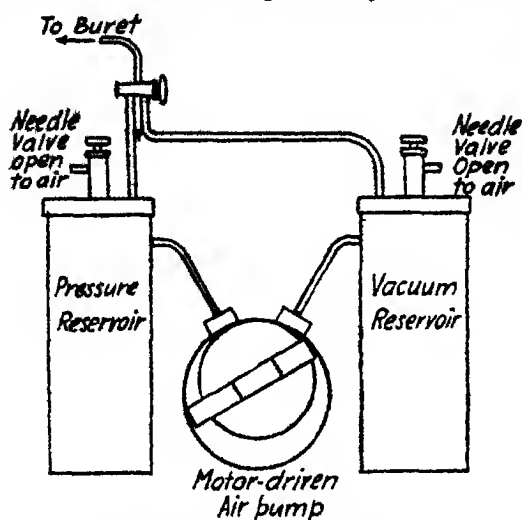


Fig. 2.—Pressure system for operating weight buret.

the effect of impurities upon the surface tension of the mercury and the height of the meniscus; (4) running past the point of contact, the amount of the error depending upon the speed of flow of the mercury, the time required for the miniature lamp to come to incandescence, and the reaction time of the observer. Errors in adjusting the mercury levels affect the measurement in 3 ways, (a) by destroying the equality of pressure between the compensator and measuring bulb, (b) by changing the volume of the compensator, and (c) by including in the compensating tube mercury which should have been run into B and weighed, or *vice versa*. If exactly the same procedure is always employed, these errors of adjustment are likely to be very nearly the same in successive measurements and, therefore, tend to cancel out when the measurements are compared.

3. Errors in collecting the mercury because of small drops adhering to the glass, small gas bubbles trapped in Tubes 1 and 3 which vary in size with variations of static pressure, and errors of weighing.

4. Errors due to changes of temperature of the system as a whole. Since comparative measurements only are wanted in most work, no error of this class occurs if the temperature is the same when each of the measurements is made. These include (1) change in the density of the mercury because of thermal expansion; (2) change in the volume of the compensator because of the thermal expansion of the glass; (3) change in the relative pressures in measuring bulb and compensator due to differences in the levels of p and p' ; (4) errors due to differences in the coefficients of ex-

pansion of the gas in compensator and measuring bulb when the composition of the two is not the same. The first 2 sources of error in this group are easily corrected for if the temperature change is known. The following equation applies:

$$V_0 - V_1 = \frac{W (t_1 - t_0)(C_m - C_g)}{d}$$

where V_1 and V_0 are, respectively, the volume of the gas determined at t_1 and the volume which would have been determined had the measurement been made at t_0 ; W is the weight of mercury observed, d is the density of mercury at the temperature of measurement, and C_m and C_g are the coefficients of expansion of mercury and glass, respectively.

5. Errors due to differences of temperature in different parts of the system. These may be (1) local temperature differences in the water bath; (2) a difference in temperature between the mercury in A and the water bath which will disappear if enough time elapses after the introduction of the mercury, and (3) a difference in temperature between the bath and the outside air which principally affects the portion of the compensating tube leading to Stopcock *g*.

6. Errors due to the fact that the liquid unavoidably present on the surface of the mercury in the buret does not have the same vapor pressure as the water in the compensator.

Experiments to Determine Accuracy of Measurement.

For the purpose of determining directly the aggregate effect which may be expected from the many possible sources of slight error encountered, 2 series of experiments were made. In the first series the same mass of gas, confined over mercury, was repeatedly measured, being entirely transferred to a mercury-sealed receiver between each consecutive pair of measurements. In the second series, a mass of gas was measured as a whole and was then subdivided, each portion measured being discarded after measurement. In both cases a little pure water was used to saturate the gas in both buret and compensator.

A typical series of measurements of the first class is shown in Table I, in which the first column gives the temperature of the water jacket, the second gives the weight of mercury actually observed, the third gives the weight of mercury corrected only for thermal expansion as described above, the fourth gives the volume of gas computed from the corrected weight of mercury, and the fifth gives the difference between each measurement and the average of all the measurements.

Table II gives a summary of all the results obtained in the last 14 comparisons by the method illustrated in Table I. A large number of other comparisons were made with results nearly but not quite so concordant. Just previous to making the first comparison given in the table a minor

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TABLE I
Typical Set of Measurements of a Single Volume of Gas.

Temperature °C	Weight of mercury		Volume Cc	Deviation from average Cc
	Observed G	Corrected G		
18 7	1130 10	1130 10	83 405	-0 006
18 8	1130 16	1130 17	83 411	0 000
18 9	1130 10	1130 14	83 408	-0 003
19 1	1130 09	1130 16	83 410	-0 001
19 1	1130 26	1130 33	83 423	+0 012
19 2	1130.06	1130 15	83 409	-0 002
19 5	1129 96	1130 10	83 405	-0 006
19 6	1130 05	1130 21	83 414	+0 003
19 6	1130 10	1130 17	83 411	-0 000
Average volume 83 411				
Average deviation from average			± 0 0017 cc	
			0 0044 %	
Greatest deviation from average			0 012 cc.	
			0 014 %	

alteration in the construction of the apparatus was made which is believed to have slightly improved its accuracy, hence the results here given represent all the comparisons of this kind made with the apparatus as described.

TABLE II

Volume measured Cc	Number of measure- ments	Average deviation from average		Greatest deviation from average		No of measurements deviating as much as 0 01 cc
		%	Cc	%	Cc	
98 910	7	0 006	0 006	0 014	0 014	2
88 349	4	0 005	0 004	0 008	0 007	0
87 329	10	0 005	0 004	0 014	0 012	1
85 519	4	0 001	0 001	0 002	0 002	0
83 411	9	0 004	0 004	0 014	0 012	1
83 306	9	0 006	0 005	0 014	0 012	1
81.388	7	0 004	0 004	0 009	0 008	0
77 261	4	0 007	0 005	0 009	0.007	0
75 498	4	0 002	0 002	0 002	0 002	0
28 453	3	0 009	0 003	0 014	0 004	0
8 474	7	0 033	0 003	0 070	0 006	0
3 129	3	0 019	0 006	0.028	0 0009	0
1 413	2	0 026	0 0004	..	.	0
0 220	3	1 1	0 0024	1.8	0 0041	0
Total	76			...		5

General average deviation of individual readings from average determination of same volume, 0 0034 cc.

In Table III are given the results obtained by measuring a volume of gas, then subdividing it into a number of portions each of which is measured. If there were any considerable systematic error it would be indicated by a difference between the measurement of the volume as a whole and the sum of the measurements of the partial volumes.

TABLE III.

Partial volumes measured.....	23.852	8.468	10.800	1.201
	24.942	11.379	5.268	0.219
	28.443	8.589	20.791	
			29.671	
			7.647	
			24.690	
Sum.....	77.237	28.436	98.867	1.420
Direct determination of total volume ...	77.244	28.443	98.881	1.413

The data presented in the above tables indicate a percentage accuracy on a sample of 100 cc. which is comparable with the accuracy of good titrimetric determinations.

Since the size and shape of the container in which the gas is measured are determined only by convenience, the method is obviously suited to the measurement of much larger volumes of gas than were here determined. Water can, of course, be used as the confining liquid with the usual limitations on account of solubility.

The apparatus can also be easily adapted as an accurate and convenient gas volumeter for determining the amount of gas evolved from a solid or liquid by any chemical reaction. For this purpose the weight of sample taken and the amount of gas confined in the compensator may be so related that the weight of confining liquid will be a simple multiple of the percentage of the constituent to be determined.

Summary.

An apparatus for conveniently determining small quantities of gas by weighing the confining liquid displaced is described and its percentage accuracy is shown to be comparable with the general accuracy of good titrimetric measurements.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, ORDNANCE DEPARTMENT.]

THE ENTROPY OF GASES.

BY RICHARD C. TOLMAN.

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From a thermodynamic point of view, the problem of chemical affinity may be considered as completely solved, as soon as we have determined the heat content and the entropy content of all the reacting substances in which we are interested. The solution of this important task has been greatly simplified by the work of Nernst and Planck in introducing the so-called third law of thermodynamics, which states that the entropy content of solids and liquids becomes zero at the absolute zero of temperature. This has made possible a determination of the entropy content of *solids and liquids* at any temperature merely from a knowledge of specific

heat data. The next step in this field of thermodynamic chemistry is a consideration of the underlying principles determining the entropy of gases and solutes.

Considerable theoretical speculation on the problem of the entropy of monatomic gases, or on the equivalent problem of determining Nernst's so-called chemical constants, has already been done by Sackur,¹ Tetrode,² Stern,³ Keesom,⁴ Nernst,⁵ Ratnowsky⁶ and Lindemann.⁷ These investigators have obtained a considerable measure of agreement in their conclusions in spite of the fact that they have based their work on a variety of assumptions which are hard to disentangle, and sometimes conflicting. Comparisons of experimental data with the results of these theoretical predictions have been made by Nernst⁸ and Egerton.⁹

The purpose of the present paper is first to derive an equation for the entropy of a monatomic gas in a new and very simple way, making use of the author's theory of similitude,¹⁰ and then to compare the predicted results with the relatively accurate values of the entropies of the elements which have been presented by Lewis and Gibson.¹¹ It should be noted in this connection that the entropy values of Lewis and Gibson have been obtained from plots of actual specific heat data and hence provide a more satisfactory basis of comparison than was available to Nernst¹² and Egerton.

1. General Equation for the Entropy of a Perfect Monatomic Gas.—

Since the heat capacity per mol at constant pressure for a perfect monatomic gas is exactly equal to $(5/2)R$ and the heat absorbed when the pressure is changed reversibly at temperature T from p_1 to p_2 is exactly equal to $RT \ln(p_1/p_2)$, we can evidently write as an expression for the entropy of a perfect monatomic gas at temperature T and pressure p ,

$$S = S_1 + 5/2 R \ln T - R \ln p, \quad (1)$$

where S_1 is the entropy of the gas at unit temperature and unit pressure.

An examination of this equation shows that the problem of determining

¹ Sackur, *Ann. phys.*, 36, 598 (1911), 40, 67 (1913).

² Tetrode, *ibid.*, 33, 434 (1912).

³ Stern, *Physik. Z.*, 14, 629 (1913); *Ann. Phys.*, 44, 497 (1914).

⁴ Keesom, *Physik. Z.*, 15, 217 (1914).

⁵ Nernst, *Ver. deut. physik. Ges.*, 18, 83 (1916).

⁶ Ratnowsky, *ibid.*, 18, 263 (1916).

⁷ Lindemann, *Phil. Mag.*, 38, 173 (1919); 39, 21 (1920).

⁸ Nernst, "Die Theoretischen und Experimentellen Grundlagen des neuen Wärmesatzes" (1918).

⁹ Egerton, *ibid.*, 39, 1 (1920).

¹⁰ Tolman, *Phys. Rev.*, 3, 244 (1914); 4, 145 (1914); 6, 219 (1915); 8, 8 (1916); 9, 237 (1917).

¹¹ Lewis and Gibson, *THIS JOURNAL*, 39, 2354 (1917).

¹² A number of additional gases other than those considered by Nernst and Egerton will be treated in this paper.

the entropy of perfect monatomic gases will be completely solved as soon as we have some means of predicting the value of the undetermined quantity S_1 . This quantity will obviously depend in the first place on the units of entropy, temperature and pressure employed, and in the second place may depend on the properties of the particular gas which is under consideration. Since the gases to be considered are by hypothesis both *perfect* and *monatomic*, they can theoretically consist only of non-attracting, point particles and hence such gases can differ from each other only in the mass of these point particles, *i. e.*, in their molecular weight m . Under these circumstances the only property of the gas upon which S_1 can depend is the molecular weight m . Hence we can obviously re-write Equation 1:

$$S = \phi(m) + 5/2 R \ln T - R \ln p \quad (2)$$

where ϕ is some functional relation whose form we wish to determine.

2. Application of Theory of Similitude.—The theory of similitude,¹ requires that all the general equations of physics must be completely invariant when the different physical variables contained in the equation are transformed in accordance with a particular set of transformation equations which have been developed from the theory. For the quantities involved in our equation, *i. e.*, entropy (per mol) S , mass (per mol) m , heat capacity (per mol) R , temperature T , and pressure p , the transformation equations developed from the theory of similitude are as follows:

$$S = S' \quad m = xm' \quad R = R' \quad T = xT' \quad p = x^4p' \quad (3)$$

where x may be any pure number.

Substituting in Equation 2 we obtain,

$$S' = \phi(xm') + 5/2 R' \ln xT' - R' \ln x^4p'. \quad (4)$$

In accordance with the invariance demanded by the theory of similitude the function ϕ must be of such a form that all the x 's in (4) shall cancel out, and by inspection we see that this can only be true when ϕ has the form

$$\phi(m) = R \ln a(m)^{1/5} \quad (5)$$

where a is a general constant independent of the gas. Substituting in Equation 2 we obtain as our final equation,

$$S = 3/2 R \ln m + 5/2 R \ln T - R \ln p + S_0 \quad (6)$$

where the quantity $S_0 = 3/2 R \ln a$ is a general constant independent of the particular gas.

We have thus obtained in a very simple way a general equation for the entropy of perfect monatomic gases. In a later section of the article we shall compare the available experimental data with the predictions of this equation.

¹ *Loc. cit.*

3. **Other Theoretical Methods of Attack.**—Equation 5 or its equivalent has been derived by several investigators.

Lindemann¹ has applied dimensional reasoning to the equivalent problem of determining the relation between the molecular weight m and Nernst's chemical constant C which is directly related to our quantity S_1 , and has arrived at conclusions that are in agreement with ours. It is important to point out, however, that the successful application of dimensional reasoning to this problem requires additional and arbitrary assumptions over those necessary for solving the problem by the theory of similitude. Referring again to Equation 2 we see, since S and R both have the same dimensions, that $\phi(m)$ must have the dimensions of $R \ln pT^{-1/2}$ or written in the form of a dimensional equation

$$[\phi] = [m]^{2/3} T^{-1} \ln [m]^{-1/3} T^{-1/2}.$$

Now, it is obvious that no function of m alone can have these required dimensions, and hence since we have already come to the conclusion that m is the only "dimensionable variable" entering the function $\phi(m)$, it is evident that $\phi(m)$ must also include one or more "dimensional constants." Since, however, we have no way of knowing beforehand what these "dimensional constants" may be, we have no way of solving the problem. In order to try to meet this difficulty, we could follow Lindemann¹ by making the additional assumption that the only dimensional constants involved in $\phi(m)$ are Planck's constant h and Boltzman's constant $k = R/N$ and would then find it possible to derive our final equation (6), by finding the only combination of m , h and k which has the dimensions required by Equation 7. This added assumption seems, however, relatively arbitrary and greatly reduces the value of the attempted dimensional treatment.

Sackur, Tetrode, Stern, Keesom, Nernst and Ratnowsky² have all also derived equations of the form (6) for the entropy of a perfect monatomic gas. Their work is based on a variety of assumptions which are rather difficult to disentangle and they do not come to complete agreement as to the magnitude of the universal constant which we have called S_0 ; they all agree, however, that the entropy of a monatomic gas depends on the atomic weight in the way predicted in our equation. To give a partial statement as to the kind of assumptions which they have employed, Sackur's first derivation was based on the Sommerfeld hypothesis that every element of action in the universe is some multiple of the fundamental constant of action h . In his later derivation he abandons this hypothesis on account of the fact that action is the product of two quantities, energy and time, both of which are presumably continuous in nature, and bases his conclusions on what he conceives to be a fundamental analysis of the

¹ *Loc cit.*

² *All loc cit.*

significance of h . Tetrode bases his work on the assumption that the volume σ , of the "cells of equal probability" into which we can divide the $2n$ dimensional space familiarly used in the considerations of statistical mechanics for plotting the values of the n generalized coordinates and n generalized momenta belonging to the elements of the system, can be put equal to zh where h is Planck's constant and z is a pure number. Stern's value for the entropy of a perfect monatomic gas is obtained by considering the entropy increase in heating a solid from the absolute zero to a point where Dulong and Petit's law holds, and then vaporizing. To determine the entropy increase in heating the solid he makes use of the Planck-Einstein formula for the specific heat of a solid with a single frequency of vibration and to determine the entropy of evaporation he makes use of theoretical molecular speculations. The particular and improbable assumptions as to the nature of the solid are found to disappear from the final result. Keesom, Nernst and Ratnowsky all assume a so-called "nullpunkt energie" ϵ_0 for the lower value of the energy at the absolute zero still associated with a degree of freedom of frequency ν . This "nullpunkt energie" in the Nernst treatment is in equilibrium with radiant energy in the ether. On rise of temperature, energy is drawn not only from the surroundings but also from the reservoir of "nullpunkt energie" and the principle of the conservation of energy becomes merely statistically true rather than true for the individual elements of the system. It is evident that the theories in question (like so much of quantum theory) are still in their birth-pangs. For the time being, the simple although non-mechanistic treatment afforded by the theory of similitude may prove useful.

4. Entropy of Gases in General.—The above treatment provides primarily a method for calculating the entropy of gases which are monatomic. The work of Eucken, however, has shown that hydrogen has only 3 degrees of freedom at low temperatures, and we are led to expect that all gases will behave as though monatomic at low enough temperatures. This will permit us to calculate the entropy of any gas at any temperature as soon as we obtain the necessary specific heat data bridging over the gap between very low and moderate temperatures. In the case of hydrogen such a calculation is already possible, and in the sequel we shall show the agreement between the experimental and predicted results for this gas.

5. Calculation of Results.—Returning to our fundamental equation (6), we have

$$S = \frac{3}{2} R \ln m + \frac{5}{2} R \ln T - R \ln p + S_0 \quad (6)$$

where S_0 is a constant independent of the nature of the gas. Since we shall use this equation for calculating entropies always at 25° and one

atm. pressure, T and p become constant and the equation can be rewritten for our purposes in the form

$$S_{298} = 6.87 \log m + C.$$

Helium.—We shall choose the gas helium for determining the value of C . In accordance with Lewis and Gibson,¹ we shall take $S_{298} = 29.2$ and shall take $m = 4.00$. We obtain $C = 25.1$, and may now write, for any monatomic gas of molecular weight, m ,

$$S_{298} = 6.87 \log m + 25.1. \quad (7)$$

Argon.—For argon Lewis and Gibson¹ give the value $S_{298} = 36.4$, while a substitution of $m = 40$ gives $S_{298} = 36.1$ a satisfactory check.

Mercury, Cadmium, Zinc, Platinum, Molybdenum, Tungsten.—The vapor pressures for a number of metals which give monatomic gases have been determined and expressed in the literature by a formula of the Hertz type,

$$\log p(\text{mm.}) = -A/T + B \log T + C \quad (8)$$

Assuming this formula to be accurate enough for purposes of extrapolation, it may be used for determining the change in entropy at 298° when the metal is evaporated at its vapor pressure and then compressed to one atmosphere. Changing to natural logarithms and to pressures in atmospheres we may write in place of Equation 8,

$$\ln p(\text{atm.}) = -2.3 A/T + B \ln T + 2.3 C - 2.3 \log 760. \quad (9)$$

Differentiating and substituting into the Clausius equation, $d \ln p/dT = L/RT^2$, we obtain

$$L/T = (2.3 AR/T) + BR \quad (10)$$

and this is the entropy increase when we evaporate at temperature T to form vapor at the vapor pressure p . Adding the quantity $R \ln p$, which is the increase in entropy when we change to a pressure of one atmosphere, and making use of Equation 9, we obtain,

$$\Delta S = L/T + R \ln p = BR + BR \ln T + 2.3 CR - 2.3 R \log 760.$$

Since we shall be interested in the value of ΔS at 298° absolute, we may substitute $T = 298$, $R = 1.99$ and obtain,

$$\Delta S_{298} = 13.33 B + 4.58 C - 13.65. \quad (11)$$

This equation gives us the increase in entropy when one mol of vapor at atmospheric pressure is formed from the condensed phase at 298° absolute. We may apply it to the following vapor pressure data:

Mercury.—Vapor pressure measurements by Knudsen,² between 273° and 323° absolute.

$$\log p(\text{mm.}) = (-3342.26/T) - 0.847 \log T + 10.5724.$$

¹ *Loc cit.*

² Knudsen, *Ann. phys.*, 29, 179 (1909).

Cadmium.—Vapor pressure measurements by Egerton¹ between 411.2 and 545.5° absolute:

$$\log p(\text{mm.}) = (-6060/T) - 0.5 \log T + 10.5979.$$

Zinc.—Vapor pressure measurements by Egerton,¹ between 529.8 and 636.0° absolute:

$$\log p(\text{mm.}) = (-7176/T) - 0.5 \log T + 10.9433.$$

Platinum.—Vapor pressure measurements by Langmuir and MacKay,² between 1682 and 2000 absolute:

$$\log p(\text{mm.}) = (-27800/T) - 1.26 \log T + 14.09.$$

Molybdenum.—Vapor pressure measurements by Langmuir and MacKay,² between 1994 and 2373 absolute:

$$\log p(\text{mm.}) = (-38600/T) - 1.26 \log T + 17.354.$$

Tungsten.—Vapor pressure measurements by Langmuir,³ between 2440 and 2930° absolute:

$$\log p(\text{mm.}) = (-47440/T) - 0.9 \log T + 15.502.$$

Applying Equation 11 to the above data, adding the values given by Lewis and Gibson⁴ for the entropy of the condensed phase at 298° absolute, and comparing with the results of the theoretical Equation (7), we obtain,

	Lewis-Gibson	ΔS_{298° Equation 11	S_{298° Experimental	S_{298° Theoretical.
Mercury.. . . .	17.8	23.3	41.1	40.9
Cadmium.... .	11.6	28.2	39.8	39.2
Zinc	9.8	29.9	39.7	37.6
Platinum.	10.0	33.9	43.9	40.8
Molybdenum. .	7.5	48.9	56.4	38.7
Tungsten	8.4	45.3	53.7	40.7

There is good agreement between the experimental and theoretical values of entropy except for molybdenum and tungsten. This lack of good agreement is not surprising, in view of the vapor pressure extrapolation over a range of 2000°.

Monatomic Bromine, Iodine and Hydrogen.—Free energy and entropy are connected by the equation,

$$\Delta S = (\Delta H - \Delta F)/T \quad (12)$$

where ΔS is the increase in entropy accompanying a reaction at temperature T , ΔH being the increase in heat content and ΔF , the increase in free energy. Using the nomenclature of Lewis we may write,

$$\Delta H = \Delta H_0 + \Delta \Gamma_0 T + \Delta \Gamma_1/2 T^2 + \Delta \Gamma_2/3 T^3 + \dots$$

$$\Delta F = \Delta H_0 - \Delta \Gamma_0 T \ln T - \Delta \Gamma_1/2 T^2 - \Delta \Gamma_2/6 T^3 \dots + IT$$

¹ Egerton, *Phil. Mag.*, 33, 333 (1917).

² Langmuir and MacKay, *Phys. Rev.*, 4, 377 (1914).

³ Langmuir, *ibid.*, 2, 329 (1913).

⁴ *Loc. cit.*

where I is an integration constant and the ΔT terms are dependent in a familiar way upon heat capacities. Substituting into Equation 12 we obtain,

$$\Delta S = \Delta T_0 + \Delta T_0 \ln T + \Delta T_1 T + \Delta T_2/2 T^2 + \dots - I. \quad (13)$$

This equation can be applied to the following free energy data.

Bromine.—Lewis and Randall¹ give the following free energy equation for the reaction $\text{Br(l.)} = \text{Br(g.)}$ based on dissociation measurements between 1073 and 1323° absolute.

$$\Delta F = 31425 + 3.05 T \ln T + 0.001 T^2 - 48.14 T.$$

Iodine.—Lewis and Randall² give the following free energy equation for the reaction $\text{I(s.)} = \text{I(g.)}$ based on dissociation measurements between 1073 and 1473° absolute.

$$\Delta F = 26275 + 1.60 T \ln T - 40.36 T.$$

Hydrogen.—Lewis and Randall³ give the following free energy equation for the reaction $\text{H}_2 = 2\text{H}$ based on dissociation measurements between 2500 and 3000° absolute.

$$\Delta F = 61000 - 3.5 T \ln T + 0.00045 T^2 + 20.2 T.$$

Applying Equation 13 to the above data, using $T = 298$, adding the values given by Lewis and Gibson,⁴ for the entropy of the undissociated gas at 298° absolute, and comparing with the results of the theoretical equation (7) we obtain,

		ΔS 298°. Equation 13.	S 298°. Experimental	S 298°. Theoretical.
	Lewis-Gibson.			
Bromine (Br)	18 5	27 1	45 6	38.2
Iodine (I).....	15 7	29 6	45 3	39.6
Hydrogen (H)....	15 9	1.5	17 4	25 1

The relatively poor agreement is probably due to the wide extrapolation necessary from temperatures where the equilibrium could be measured.

Diatomic Hydrogen.—As already stated, our theoretical equation not only makes possible a prediction of the entropy of monatomic gases, but since all gases become monatomic at low temperatures, permits a treatment of all gases as soon as the necessary specific heat data are available. In the case of hydrogen such data have been obtained by Eucken,⁵ Plotting Eucken's data for the specific heat of hydrogen against the logarithm of the temperature, it was found that the entropy of hydrogen (H_2) at 298° is 1.4 units greater than it would be if it had remained a monatomic gas way up to that temperature. Using our theoretical Equation (7) for the entropy of a monatomic gas and adding 1.4 we get

¹ Lewis and Randall, *This Journal*, 38, 2348 (1916).

² Lewis and Randall, *ibid.*, 36, 2259 (1914).

³ Lewis and Randall, *ibid.*, 36, 1969 (1914).

⁴ *Loc. cit.*

⁵ Eucken, *Sitzb. kgl. preuss. Akad.*, 1912, 148.

28.6 as compared with the two values of Lewis and Gibson 29.4 and 31.8, a satisfactory check, although they believe the higher value is the more reliable.

6. **Summary of Data.**—The following table presents a comparison of the experimental results for the entropy of gases at one atmosphere and 298° absolute, and the theoretical results predicted with the help of the equation,

$$S = (3/2) R \ln m + (5/2) R \ln T - R \ln p + S_0$$

$$= 6.87 \log m + 25.1 \text{ (at 1 atm. and 298° abs.)}.$$

The second column states the range of temperature over which extrapolation has to be made in order to compare the results, and these results are arranged in the order of the uncertainty introduced by this factor.

Gas.	Range over which extrapolation was made. °.	S 298°.		Diff.
		Experimental	Theoretical	
Helium.....	29 2
Argon.....	None	36 4	36 1	0.3
Mercury....	None	41 1	40 9	0.2
Hydrogen (H ₂)..	None	31 8(29 4)	28.6	3.2
Cadmium....	150	39 8	39 2	0.6
Zinc.....	300	39 7	37.6	2.1
Bromine.....	900	45 6	38 2	7.4
Iodine.....	900	45 3	39 6	5.7
Platinum..	1500	43 9	40 8	3.1
Molybdenum....	1700	56 4	38 7	17.7
Tungsten.....	2100	53 7	40 7	13.0
Hydrogen (H)....	2500	17 4	25 1	7.7

The agreement between the experimental and theoretical values is very close in cases where wide extrapolation does not have to be made and is probably within the experimental error in all cases. It should also be noted that the nature of the experimental results alone is enough to show that entropy of gases is certainly not entirely a fortuitous matter.

WASHINGTON, D. C

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF SILICON. THE ANALYSIS OF SILICON TETRACHLORIDE.

Preliminary Paper.

BY GREGORY P. BAXTER, PHILIP F. WEATHERILL AND EDWARD O. HOLMES, JR.

Received April 12, 1920.

Present knowledge of the atomic weight of silicon is in a far from satisfactory state. Even the more modern determinations of this constant vary from 28.0 to 28.4. In his "Recalculation of the Atomic Weights," Clark,¹ from a consideration of all available data, finds the value 28.25 and the value 28.3 has been adopted by the International Committee on Atomic Weights. The atomic weight of silicon is a particularly important one from a geological and mineralogical point of view, since silicates constitute so large a proportion of the earth's crust. Because of this importance, and because our preliminary experiments indicate a value quite different from the value in common use we have thought it desirable to present the results of these experiments without waiting for the completion of the research.

We chose the method which has already been used by Dumas² of comparing silicon tetrachloride with silver; for the tetrachloride is readily purified by distillation, and the comparison of a chloride with silver is one of the most accurate of analytical processes. These advantages outweigh the disadvantage of the small percentage of silicon in the tetrachloride, 16.5.

Preparation of Silicon Tetrachloride.³

One portion of the silicon tetrachloride was made by passing dry chlorine from a cylinder over hot powdered silicon and condensing the product in a flask cooled with ice. The product contained a red precipitate, presumably ferric chloride, which was easily removed by filtration through glass wool. This material, which contained an excess of chlorine, was mixed with a portion obtained from the General Electric Company, and the mixture was admitted, together with several cc. of mercury, through a separatory funnel into an exhausted flask, and the separatory funnel was sealed off. In order to eliminate the excess of chlorine, the chloride was left in contact with the mercury for a week in the exhausted flask.

The impurities chiefly to be feared in this material were decomposition products resulting from hydrolysis, *i. e.*, silicic acid and hydrochloric

¹ *Smithsonian Inst. Pub.*, "Constants of Nature," Part V, p. 278 (1910).

² *Ann. chem. pharm.*, 113, 31 (1860). Schiel also determined the chlorine in silicon tetrachloride as silver chloride, *ibid.*, 120, 94 (1861).

³ The preparation and distillation of silicon tetrachloride were carried out by Mr. Holmes.

acid, besides silicon hexachloride, carbon tetrachloride and titanium tetrachloride. Since the boiling point of silicon tetrachloride is 58° and those of the last 3 substances are $144-8^{\circ}$, 76.5° and 136° , respectively, it seemed reasonable to hope that the silicon tetrachloride could be effectively purified by fractional distillation. Such a process was carried out at low temperatures by condensing the chloride at the desired point by means of either liquid air or a carbon dioxide-alcohol mixture.

The exhausted flask, to which was attached a special valve such as was used by Briscoe¹ and later by Baxter and Starkweather,² was sealed to a system of 3 small bulbs and a flask to which also a special joint had been attached. After this system had been evacuated, the special joint attached to the first flask was opened by breaking the capillary, and then the 3 bulbs and finally the flask were successively filled with silicon tetrachloride by chilling, each bulb being sealed off as soon as nearly filled. Approximately $\frac{1}{4}$ of the chloride was left in the original flask and rejected. The more volatile portions, which it was hoped contained the bulk of the hydrochloric acid, were collected in the 3 small bulbs and also were discarded.

The flask containing the partially purified tetrachloride was now attached to a system consisting of one large bulb, 14 small ones and a liter reservoir. After this system also had been carefully evacuated, connection with the flask containing the tetrachloride was made by breaking the capillary in the special joint. The reservoir was first sealed off and then about $\frac{4}{5}$ of the liquid was distilled into the first bulb. The bulb containing the residue was next sealed off, and then the small bulbs were successively filled with the tetrachloride and sealed off.

The distillation apparatus was constructed wholly of glass and resembled very closely that used by Baxter and Starkweather in the preparation of tin tetrachloride.³

Method of Analysis.³

After being weighed the bulb containing silicon tetrachloride was broken under excess of sodium hydroxide and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a solution of a weighed very nearly equivalent amount of pure silver. The point of exact equivalence between chloride and silver was then found with the assistance of a nephelometer.

Water, nitric acid and silver were purified by the usual methods where extreme refinement is necessary.⁴ To prepare sodium hydroxide free

¹ *J. Chem. Soc.*, 107, 63 (1915).

² *Proc. Nat. Acad. Sci.*, 2, 718 (1916); *THIS JOURNAL*, 42, 907 (1920).

³ The analytical operations were performed by Mr. Weatherill.

⁴ See for instance Baxter and Grover, *THIS JOURNAL*, 37, 1028 (1915).

from chloride, the best commercial material was precipitated with a slight deficiency of barium hydroxide to eliminate the greater part of the carbonate, and after the precipitate had been thrown out by centrifugal whirling, the clear solution was evaporated to crystallization in a platinum dish. The crystals were centrifugally drained and rinsed and then were twice more crystallized in the same way. The product was free from chloride.

The bulb was cleaned by means of sodium hydroxide and cleaning solution. Then it was rinsed, dried with a lintless cloth and left in a desiccator for some hours before being weighed by substitution. Simultaneously with the weighing, the temperature, pressure and humidity of the balance room were observed. Next the bulb, suspended in a platinum wire basket, was weighed under water and its volume calculated from the weight of water displaced.

The bulb, with a solution of about 50% excess of the quantity of sodium hydroxide necessary to react completely with the tetrachloride, was placed in a heavy-walled glass-stoppered flask, and by shaking the flask the bulb was broken. In order to avoid loss of silicon tetrachloride or hydrochloric acid vapor, the flask was allowed to stand closed for some time. Then it was opened, and after dilution of the solution to one liter, the glass was collected upon a quantitative filter, the solution being received in a large glass-stoppered precipitating flask or bottle. Gentle ignition below the melting point of glass in a weighed platinum crucible eliminated the filter.

The weight of glass determined in this way was found in 5 experiments to be slightly too large. In these experiments a weighed empty bulb was broken under a similar solution of silicon tetrachloride in sodium hydroxide, and then the glass was collected on a filter, washed with cold water, and ignited in an identical fashion. The average excess in weight was 0.20 mg., the largest being 0.34 mg. and the smallest 0.14 mg. A correction of 0.20 mg. has, therefore, been subtracted from the weight of glass found in each of the analyses. A vacuum correction of +0.00034 g. per gram of glass also has been applied.

The weight of the bulb was corrected to vacuum by computing the weight of air displaced by the bulb and weights, with due consideration of the atmospheric conditions at the time of weighing.

As soon as the alkaline solution had been filtered it was made slightly acid with nitric acid, for such acid solutions remain perfectly clear for long periods. From the weight of silicon tetrachloride the necessary amount of silver was computed, and this quantity of the purest silver was weighed out and dissolved in nitric acid. Both solutions having been diluted until approximately 0.1 *N* (except in Analysis 1), the silver solution was slowly added to the chloride, and the mixture was thoroughly

shaken and allowed to stand several days with occasional shaking. The clear supernatant liquid was next tested for excess of chloride or silver in a nephelometer and if a deficiency of either was found, a suitable amount of a 0.01 *N* solution of silver nitrate or potassium chloride was added and the shaking and testing were repeated. The process was continued until the amounts of chloride and silver were equivalent.

The weight of silver has been corrected to vacuum by subtracting 0.031 mg. per gram of metal. The atomic weights of silver and chlorine were assumed to be 107.880 and 35.457 respectively.

In the table the fractions are numbered in the order in which the bulbs were filled. In Analysis 1 the solutions were considerably more concentrated than 0.1 *N* when precipitation was carried out. The apparent effect of this was the occlusion by the precipitate of some of the chloride which slowly leached out, so that the end-point was not finally reached for some weeks. If this leaching out was not complete it would account for the somewhat higher result of this experiment. On the whole, however, the different fractions show no positive evidence of dissimilarity.

Number of analysts	Fraction of SiCl_4	Weight of SiCl_4 in vacuum Grams	Weight of silver in vacuum Grams	Weight of silver added in solution Gram	Corrected weight of silver in vacuum Grams	Ratio SiCl_4 4 Ag.	Atomic weight of silicon
1	12	10 43530	26 47403	0 02120	26 49523	0 393856	28 129
2	3	5 97853	15 17909	0 00395	15 18304	0 393764	28 089
3	9	8 79053	22 31981	0 00150	22 32131	0 393814	28 112
4	6	6 83524	17 35557	0 00060	17 35617	0 393828	28 114
Average, 0 393815							28 111

While we wish to emphasize the fact we do not consider the evidence presented as final, it seems to indicate that the atomic weight of silicon is not far from 28.1 instead of the value 28.3 as now accepted by the International Committee on Atomic Weights.

(CAMBRIDGE, MASS.)

[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY OF THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE CHEMICAL COMPOSITION OF COTTONSEED OIL.

BY GEORGE S. JAMIESON AND WALTER F. BAUGHMAN.

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Although cottonseed oil has been an important article of commerce for a great many years, neither its qualitative nor quantitative chemical composition has been definitely established. Investigators agree that palmitic acid is the predominating saturated acid but the presence of stearic and arachidic acids has been asserted and denied. Hehner and Mitchell¹ found 3.3% of stearic acid in cottonseed oil stearine. Meyer²

¹ Hehner and Mitchell, *Analyst*, 21, 328 (1896).

² Meyer, *Chem. Ztg.*, 31, 793 (1907).

fractionally distilled *in vacuo* the methyl esters of the insoluble acids and then separated the saturated and unsaturated acids in the 2 highest boiling fractions by the lead salt ether method. By fractional crystallization from alcohol he obtained from the saturated acid portion a small quantity of an acid melting at 63–73° which he believed to be a mixture of stearic acid and arachidic acid. Lewkowitsch¹ states that "recent investigations by the author have shown that it is doubtful whether stearic acid does occur in cottonseed oil," and also that "small quantities of arachidic acid appear to be present."

Our knowledge of the composition of the unsaturated acids is not so uncertain. Hazura² after demonstrating the absence of linolenic acid and the presence of linolic and oleic acids, calculated the proportions of linolic and oleic acids from the observed iodine value of the unsaturated acids (143.0) and the theoretical values for linolic and oleic acids (181.4 and 90.0). He gave the approximate composition of the unsaturated acid as 60% linolic and 40% oleic. However, Lewkowitsch¹ gives the results of Farnsteiner, who found by direct experiment only 23.9% of linolic acid in the unsaturated acids. The calculated iodine value of a mixture of 23.9% linolic acid and 76.1% oleic acid is only 112.

In view of these conflicting statements in regard to the composition of cottonseed oil, it was thought well worth while to investigate this problem again.

The oil used in this investigation was cold pressed from one bushel of Sea Island cottonseed by means of an oil expeller. The lead salt ether method showed that it contained 23.0% of saturated acids and 72.5% of unsaturated acids. The iodine value (Hanus) of the unsaturated acids was 142.2, the saponification value 199.4 and the mean molecular weight, 281.3.

Examination of Unsaturated Acids.—Refined oil was used for the preparation of the unsaturated acids in order to obtain them uncontaminated with mucilaginous material, etc.

The bromine addition derivatives were prepared according to the method of Eibner and Muggenthalor³ which is briefly as follows.

To the acids dissolved in dry ether and cooled to -10° , bromine is added slowly, after which the mixture is allowed to stand for 2 hours at -10° . Hexabromide, the bromo derivative of linolenic acid, is insoluble in ether. No precipitate insoluble in ether was obtained, which confirms the observations of previous investigators that cottonseed oil contains no linolenic acid. The excess of bromine was removed from the

¹ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., 2, 197.

² Hazura, *Z. angew. Chem.*, 1888, 315.

³ Lewkowitsch, *ibid.*, 1, 573.

etheral solution by washing it in a separatory funnel with an aqueous solution of thiosulfate. After removing all traces of water from the washed ether solution, the ether was removed by distillation and the residue boiled with 250 cc. of petroleum ether. The petroleum ether solution was allowed to stand in the ice box overnight and then the linolic tetrabromide was removed by filtering through a weighed Gooch crucible. The filtrate was reduced to about half its original volume by distillation, cooled again in the ice box and a second crop of tetrabromide crystals obtained which was likewise removed by filtration through a Gooch crucible. The filtrate was then evaporated to dryness and weighed. The bromine content of the residue was determined by boiling a small sample with conc. nitric acid and silver nitrate. Linolic tetrabromide contains 53.33% of bromine, and oleic dibromide 36.18%, and it is a simple matter to calculate algebraically the proportion of tetrabromide and dibromide in the residue if we know the per cent. of bromine present.

The data of the analyses of the bromo derivatives are given below:

	G.
Sample of unsaturated acids.....	2.6058
Linolic tetrabromide insoluble in petroleum ether, m. p. 113-114°..	1.7619
Residue (dibromide and tetrabromide).....	3.1298
Bromine content of residue.....	43.11%
Dibromide in residue 39.59% or.....	1.8650
Tetrabromide in residue 40.41% or.....	1.2648
Total tetrabromide found.....	3.0267
Linolic acid equivalent to tetrabromide 1.4124 g. or.....	54.20%
Oleic acid equivalent to dibromide 1.1899 g. or.....	45.66%

The percentages of linolic and oleic acids in the unsaturated acids are converted into percentages of glycerides in the original oil as follows:

	Found. %.	Calculated to bases of 100%. %	Original oil. %.	Glycerides in original oil. %.
Oleic acid.....	45.66	45.72	33.15	34.64
Linolic acid.....	54.20	54.28	39.35	41.13
Total.....	99.86	100.00	72.50	75.77

A duplicate experiment gave 45.84% oleic acid and 54.16% linolic acid. The theoretical iodine value of a mixture consisting of 45.72% of oleic acid and 54.28% of linolic acid is 139.6, which agrees fairly well with the observed iodine value of the unsaturated acids (142.2).

In this connection it may be well to point out that the low results obtained for linolic acids when this method has been used by other investigators, not only for the examination of cottonseed oil but also for other oils, is due to the fact that they have considered the tetrabromide that crystallized out from the petroleum ether solution to represent the entire amount of linolic acid present, but it has been the experience of the

authors that a considerable amount remains in solution with the dibromide. This is no doubt due to the formation of an isomeric liquid tetrabromide soluble in petroleum ether and melting at 57-58° as pointed out by Rollet,¹ Matthes and Boltze² and Takahashi.³ Thus it is necessary to determine the bromine content of the residue left after evaporating off the petroleum ether and to calculate the proportions of tetrabromide and dibromide present.

Examination of the Saturated Acids.—The saturated acids were prepared from the crude oil by the lead salt ether method and esterified by dissolving in absolute methyl alcohol, saturating the resulting solution with dry hydrogen chloride and then heating under a reflux condenser for 15 hours. The ester layer was then separated from the alcohol layer, dissolved in ether and the solution washed first with water and finally with a dilute solution of sodium hydrogen carbonate. The ethereal solution was then dried with anhydrous sodium sulfate after which the ether was removed by distillation.

The mixture of methyl esters, which weighed 111 g. was subjected to fractional distillation under diminished pressure. The temperatures and pressures maintained during the distillation and the weights of the fractions are given in Table I. As indicated in the table, a preliminary

TABLE I.—COTTONSEED OIL.
Fractional Distillation *in vacuo* of Methyl Esters of Saturated Acids.
111 G. Esters Subjected to Distillation

Fraction.	Temperature °C	Pressure, Mm.	Weight, G.
	1 170-171	5	23.50
	2 171 5-173	6 5	22 05
Preliminary distillation	3 173-174	7 0 6 5	23.55
	4 174-179	7 0 6 5	(22 85)*
	5 179-190	6 5	(11 90)*
Fraction 4 redistilled	6 165-170	5 5 4 0	20 45
Fraction 5 added to residue and distillation continued	7 167 quickly rose to 170 170-175	5 0 4 5	10.85
	8 175 quickly rose to 178 178-188	4.5	2.90
	9 181-191	4.5	2.80
Residue from preliminary distilla- tion added to residue and dis- tillation continued.....	10 191 quickly rose to 194 194-235	4.5	3.50
Residue.....			0.95
Total.....			110 55

* Not included in total.

¹ Rollet, Hoppe-Seyler, *Z. physiol. Chem.*, 410, 421 (1909).

² Matthes and Boltze, *Arch. pharm.*, 250, 225 (1912).

³ Takahashi, *C. A.*, 13, 1583 (1919).

distillation was made first, resulting in 5 fractions and a residue which remained in the distilling flask. Fraction 4 was then transferred to a smaller flask and redistilled. This distillate is designated as Fraction 6. Original Fraction 5 was then added to the residue in the small distilling flask and distilled into 2 fractions, numbers 7 and 8. The residue in the large distilling flask which remained after the preliminary distillation was then added to the residue in the small flask and distilled. Two fractions were collected, numbers 9 and 10, and a small residue remained in the flask. Thus the esters of the saturated acids were divided into 8 fractions and a residue.

The iodine numbers (per cent. of iodine absorbed) and the saponification values (mg. of potassium hydroxide required to saponify one g. of the esters) of the various fractions were determined with the results given in Cols. 2 and 3, Table II. The iodine numbers are a measure of the

TABLE II.—COTTONSEED OIL.

Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated Acids.

Fraction	Iodine number.	Saponification value.	Mean molecular weight	Unsaturated		Mean molecular weight of esters of saturated acids	Myristic Acid.		Palmitic Acid		Stearic Acid		Arachidic Acid.	
				%.	G.		%.	G.	%	G.	%.	G.	%.	G.
1	3.2	208.6	268.9	2.25	0.53	268.4	6.25	1.47	86.30	20.28
2	3.5	206.8	271.2	2.46	0.54	270.8	.	.	90.73	20.00	1.65	0.36
3	5.0	205.8	272.6	3.52	0.83	271.8	.	.	86.43	20.35	4.92	1.16
6	6.0	205.4	273.1	4.22	0.86	272.2	.	..	84.47	17.27	6.18	1.26
7	11.6	202.4	277.2	8.16	0.88	275.8	.	.	69.66	7.56	17.12	1.86
8	20.2	195.6	286.8	14.21	0.41	285.4	.	.	37.17	1.08	43.73	1.27
9	21.8	192.2	291.9	15.34	0.43	291.3	.	..	20.18	0.56	59.68	1.67
10	19.7	179.0	313.4	13.86	0.48	316.0	30.25	1.06	51.40	1.80
Residue:														
	21.6	170.9	329.2	15.19	0.14	335.3	80.44	0.76
Total.....				5.10			1.47		87.10		8.64		2.56	

contaminating unsaturated acids¹ and it is possible to calculate the per cent. of esters of unsaturated acids in each fraction. Thus the iodine number of the free unsaturated acids is 142.2 from which we calculate the iodine number of the methyl esters of the unsaturated acids to be 135.4. The per cent. of esters of unsaturated acids in a fraction is given by the formula, $a \times 100/135.4$, in which a is the iodine value of the fraction. In Col. 5 and 6 of Table II are given the percentages and weights of unsaturated acid esters in each fraction.

If we calculate the number of mg. of potassium hydroxide required to

¹ It is not possible to effect a complete separation of the saturated and unsaturated acids by the lead salt ether method, and therefore the saturated acids so prepared are always contaminated by small amounts of unsaturated acids.

saponify the unsaturated acid esters in one g. of each fraction (per cent. of unsaturated acid esters multiplied by the saponification value of unsaturated acid esters (190.0)) and subtract from the saponification value of each fraction we have the number of mg. of potassium hydroxide required to saponify the saturated acid esters in one g. of each fraction. Dividing this by the per cent. of saturated acid esters in the fraction gives the saponification value of the saturated acid esters from which the mean molecular weight of the esters may be calculated, using 56.1 as the molecular weight of potassium hydroxide. This method of calculation has been more fully explained in a former paper.¹

In Col. 7 are given the mean molecular weights of the methyl esters of the saturated acids in the various fractions. Inspection of these results indicates the possible saturated acid esters that may be present. The mean molecular weight of the saturated acid esters in Fraction 1 is 268.4, which is lower than methyl palmitate (270.3) and higher than methyl myristate (242.3), and suggests, therefore, that Fraction 1 contains a mixture of these 2 esters. The mean molecular weights of the saturated acid esters of Fractions 2-9, inclusive, lie between the values for methyl palmitate and methyl stearate (298.4), and indicate, therefore, mixtures of these 2 esters. The mean molecular weight of the saturated acid esters of Fraction 10 (316.0) indicates a mixture of methyl stearate and methyl arachidate (326.4). It will be observed that the value for the residue is somewhat higher than the molecular weight of methyl arachidate. However, the residue contained some products of decomposition, the effect of which is to lower the saponification value and raise the calculated mean molecular weight.

In order to test the correctness of these deductions, the next step in the investigation was to isolate the acids from the various fractions and establish their identity by melting-point determinations and analyses. The free acids were recovered and fractionally crystallized from 95% alcohol until constant melting points were obtained. The following acids were identified:

Arachidic Acid, $C_{20}H_{40}O_2$, m. p. 77° .—From the residue an acid was obtained melting between 76° and 77° . Elementary analysis² gave the following results:

Calc. for arachidic acid: H, 12.91; C, 76.85. Found: H, 12.92; C, 76.72

No other saturated acid could be detected in the residue.

From Fraction 10 there was obtained an acid melting at $76-76.5^\circ$ which gave the following results on analysis.³

Found: H, 12.98; C, 76.93.

¹ THIS JOURNAL, 42, 152 (1920).

² Analysis by Chas. E. F. Gersdorff.

Stearic Acid, $C_{18}H_{36}O_2$, m p. 69° .—The Fraction 10 mother liquor from the arachidic acid crystallization was concentrated and an acid obtained melting at $68-69^\circ$. Upon analysis¹ the following results were obtained:

Calc for stearic acid H, 12.76, C, 75.98 Found H, 12.85, C, 76.03

Palmitic Acid, $C_{16}H_{32}O_2$, m p 62.6° .—From Fractions 2 and 3 large quantities of an acid melting at 62.5° were readily isolated. This together with the boiling points of the fractions is sufficient proof of the identity of the acid.

Myristic Acid, $C_{14}H_{28}O_2$, m p 53.8° .—As before pointed out, the mean molecular weight of the saturated acid ester of Fraction 1 (268.4) is lower than methyl palmitate, which suggests the presence of the ester of the next lower acid of the series, methyl myristate. In order to obtain a fraction richer in methyl myristate, that part of Fraction 1 which remained after taking out the portions for saponification value and iodine number determinations was redistilled *in vacuo* and 2 fractions collected as indicated below.

Fraction	Pressure Mm	Temperature °C	Weight of fraction G	Mean molecular weight
a	13	186-187	8.2	265.0
b	13	187-188		
	8	176-178	15.3	269.6

It will be noted that the mean molecular weight of Fraction a is lower and of Fraction b higher than that of the original Fraction 1.

Fraction a was again redistilled at a pressure of 4.5 mm. and 2 fractions a' and a'' collected. The free acids, recovered from the lower boiling fraction a' (weight 2.4 g.) were subjected to fractional crystallization from 95% alcohol. A fraction was obtained having a melting point of $53.5-54.0^\circ$ which was not changed by further crystallization. The fraction was not large enough for an elementary analysis. However, the evidence at hand proves quite conclusively that it was myristic acid.

It is now established that the saturated acid esters in Fraction 1 are methyl myristate and methyl palmitate while Fractions 2-9, inclusive, contain methyl palmitate and methyl stearate. Fraction 10 contains methyl stearate and methyl arachidate and the residue methyl arachidate. Using the mean molecular weight of the saturated acid esters and the theoretical molecular weights of the esters present in each fraction it is possible to calculate the percentages and amounts of the acids present in each fraction. This has been done with the results given in Cols. 8-15, Table II.

¹ Analysis by Chas. E. F. Gersdorff

E. K. NELSON.

TABLE III.—COTTONSEED OIL.
Composition of the Saturated Acids.

	G	%	Original oil. %	Glycerides in original oil. %
Myristic acid.....	1.47	1.40	0.32	0.34
Palmitic acid.....	87.10	83.06	19.10	20.04
Stearic acid.....	8.64	8.24	1.90	1.98
Arachidic acid.....	2.56	2.44	0.56	0.58
Oleic acid	5.10	4.86	0.51	0.53
Linolic acid }			0.61	0.64
Total.....	104.87	100.00	23.00	24.11

Table III gives, in Col. 2, the percentage composition of the saturated acids, in Col. 3, the percentages present in the original oil, and in Col. 4, the percentages of glycerides in the original oil.

Summary.

A study has been made of the composition of a sample of cottonseed oil, the results of which are given below:

COMPOSITION OF COTTONSEED OIL.

	%
Glycerides of { Myristic acid... ..	0.3
{ Palmitic acid... ..	20.0
{ Stearic acid.....	2.0
{ Arachidic acid.. ..	0.6
{ Oleic acid.....	35.2
{ Linolic acid.... ..	41.7
Total.....	99.8

WASHINGTON, D. C.

[CONTRIBUTION FROM THE ESSENTIAL OILS LABORATORY, DRUG DIVISION, BUREAU OF CHEMISTRY.]

THE COMPOSITION OF OIL OF CHENOPODIUM FROM VARIOUS SOURCES.

By E. K. NELSON.

Received February 28, 1920.

Since the oil of chenopodium, or American wormseed, has become the standard remedy for hookworm disease, the demand for it has increased considerably. In the producing region, Carroll county, Maryland, there are at least 7 distilling plants in operation during the season.

During October, 1919, authentic samples were collected by the author from 5 of these distilling plants, for the purpose of studying the variations in the product.

As pointed out by Schimmel and Co.,¹ the distillation of chenopodium

¹ Report of Schimmel and Co., April, 1908.

oil requires special precautions, for the reason that ascaridole, the valuable and chief ingredient, is unstable, and is decomposed gradually on boiling with water. Consequently, the distillation must be carried on rapidly with steam at a good pressure, the condenser kept warm, and the warm distillation water separating from the oil in the receiver, discarded.

The examination of these samples comprised a determination of their physical constants and an estimation of the amount of ascaridole present in them. No difficulty was encountered in obtaining ascaridole of constant boiling point by fractionating oil of chenopodium under diminished pressure. This is contrary to the findings of Hamilton and Hall.¹ Evidently these investigators either did not have a true chenopodium oil, or, as seems more probable, allowed the oil to become overheated in the bath, thus causing decomposition and loss of part of the ascaridole.

As pointed out by Schimmel and Co. and by the writer, ascaridole suffers a molecular rearrangement when heated to 150°. In carrying out a fractional distillation of the oil, it is, therefore, necessary to maintain the bath at as low a temperature as possible, never allowing it to reach 150°. Most of the distillations involved in the work herein described were carried out at 3 to 6 mm. pressure. During the distillation of the ascaridole fractions, a bath temperature of 115°, and during that of the terpene fraction, one of 80°, was found sufficient to maintain an even distillation.

The first distillation gave a very good separation of the terpenes from the ascaridole, and only 2 fractionations were required to yield ascaridole of constant boiling point. The estimation of ascaridole in this way gives results somewhat low, as it is difficult to recover all of the ascaridole from the lower fraction.

When chenopodium oil is properly made the residue on fractionation will be small, but if it has been manufactured with low pressure steam and without the precautions above mentioned, the percentage of ascaridole and the specific gravity will be low and an excessive distillation residue, which is evidently a product of the decomposition of ascaridole, will be found.

In the samples collected by the writer in the producing district, the highest distillation residue was only 2.3%, and in 8 samples experimentally distilled with very low pressure steam the distillation residues amounted to from 7 to 25%, and the ascaridole content was very low. The amount of distillation residue, therefore, gives an idea of the care with which the oil has been made.

The distillation residue appears to consist in part of water-soluble, glycol-like substances, resulting from the hydration and rearrangement of the ascaridole molecule. This indicates that during a protracted

¹ *J. Pharmacol. Exper. Therapeutics*, 11, 231 (1918).

distillation with low-pressure steam a part of the ascaridole must be decomposed and the soluble products in part pass away in the condensation water.

A very simple test of the purity of the ascaridole fractions was found in the readiness with which a few drops will ignite when poured on an electric hot plate heated to about 250°.

In addition to the authentic samples collected by the writer, 7 in number, the following specimens were also examined.

An oil from chenopodium grown and distilled in Buitenzorg, Java, received through the Bureau of Plant Industry.

Two samples distilled from wild chenopodium growing around Orlando, Florida, one from dried and the other from green plants. These were also obtained from the Bureau of Plant Industry, having been produced under the supervision of Mr. H. L. Funk of that Bureau.

One sample distilled from wild plants in the Eastern United States, transmitted by the International Health Board.

ANALYTICAL DATA ON OIL OF CHENOPODIUM

Sample.	d_{25}^{25} .	[α] _D (100 mm tube)	Solubility in 8 volumes of 70% alcohol	Ascaridole (% by vol)		Opt rotation of as- caridole	Dist'n residue %
				By dist'n %	Calc from d %		
Samples Collected in Carroll Co, Md., Oct, 1919.							
K ₁	0.9758	-4.25°	Complete	74.81	5.2	1°	2.3
K ₂	0.9792	-3.9°	Complete	77.83	7.2	15°	1.1
D.....	0.9713	-5.5°	Complete	75.78	7.3	05°	1.1
E ₁ *.....	0.9538	-6.2°	Complete	60.70	0.1	65°	1.7
E ₂	0.9592	-6.2°	Complete	65.71	0.2	5°	1.1
Bo.....	0.9783	-3.6°	Complete	76.83	1.2	0°	0.9
Br....	0.9564	-6.5°	Complete	64.69	3.2	45°	1.4
Oil from Chenopodium Grown and Distilled in Java.							
	0.9762	+0.25°	Complete	70.81	8		1.3
Oil from Wild Chenopodium, Orlando, Florida.							
Not completely							
From dry plants.	0.9148	-7.75°	soluble	41	43		2.2
Not completely							
From green plants	0.8940	-10.25°	soluble	26	30		2.4
Oil from Wild Plants, Eastern U. S.							
	0.8922	+1.65°	Not completely soluble	20	28.8	-4.0° (exp of ter- penes + 4.15°).	
Samples Returned from Brazil, Over a Year Old.							
A.....	0.9628	-3.0°	Complete	68.73	4		2.7
B.....	0.9645	-7.5°	Complete	61.74	4		7.8
C.....	0.9470	-6.45°	Slightly turbid	56.63	4		2.8
D.....	0.9589	-6.6°	Slightly turbid	62.70	9		3.1
E.....	0.9730	-5.33°	Complete	72.79	8		9.1

* Sample of first distillation of the season.

Five oils of American origin, which had been used by the International Health Board in treating hookworm disease in Brazil. These oils were at least a year old and the results are interesting as showing the keeping qualities of the oil under varying conditions. It will be noted that the distillation residues, while higher than those found in fresh oils, are not excessive.

The United States Pharmacopeia (IX) specifies that oil of chenopodium should be soluble in 8 volumes of 70% alcohol, should have a specific gravity of 0.955 to 0.980 at 25°, and an optical rotation varying between -4° and -10° in a 100 mm. tube at 25°.

An approximate check upon the ascaridole estimation was obtained by calculating the ascaridole content of each oil from its density, assuming that the density of the terpenes is 0.8466 and that of the ascaridole 1.005, and that no other constituents are present. The resulting figure is influenced, of course, by any variations in the density of the terpene mixture, and by the amount of distillation residue, which consists, of course, neither of terpenes nor of ascaridole. The figures thus obtained will be seen to run roughly parallel with those of the direct estimation of ascaridole by distillation.

Terpenes of Chenopodium Oil.

Schimmel & Co.¹ have reported the presence of *p*-cymene in chenopodium oil, but the optical activity of the terpenes and their sensitiveness toward oxidizing agents indicate the presence of other hydrocarbons.

The terpenes were separated from the authentic samples collected in Maryland, and were found to boil at 176–178° under atmospheric pressure, after rectifying over sodium. The optical activity was $[\alpha]_D = -15.9^{\circ}$ (100 mm. tube).

A small yield of a nitrosite, melting at 155°, was obtained. This is probably the nitrosite of α -terpinene, though oxidation experiments designed to show the presence of that terpene, as well as the presence or absence of γ -terpinene, gave no satisfactory results.

l-Limonene was shown to be present by the formation of its tetrabromide, melting at 104–105°.

A residue left after oxidation of the terpenes by shaking with cold permanganate solution was almost optically inactive. Boiled with permanganate solution, it yielded *p*-hydroxy-isopropyl benzoic acid, melting at 155°, thus proving the presence of *p*-cymene.

The terpenes of chenopodium oil therefore contain *p*-cymene, *l*-limonene and probably α -terpinene.

An examination of the terpenes separated from the oil distilled from the wild plants collected in Florida showed them to be of the same character.

¹ Semi-Annual Report of Schimmel and Co., Apr., 1908, 113.

Summary.

Emphasis is placed on the necessity of carefully observing certain precautions in the distillation of chenopodium oil from the plant, in order to avoid the decomposition of the ascaridole by prolonged contact with steam or boiling water.

An examination of 7 authentic samples of chenopodium oil collected during the season of 1919 shows them to comply with the requirements of the United States Pharmacopeia and to contain from 60 to 77% of ascaridole.

The examination of a sample of chenopodium oil distilled in Java shows it to be very similar to the oils of American origin, and the analysis of 5 American oils returned from Brazil, and over a year old, shows them to be normal in character.

Chenopodium oil distilled from wild plants collected in Florida was found to contain less ascaridole than the oil distilled from cultivated plants in Maryland. The same constituents were found in it that were found in the Maryland oil.

The terpenes of chenopodium oil were found to contain *p*-cymene, *l*-limonene and probably α -terpinene.

WASHINGTON, D C

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY] REACTIONS AND DERIVATIVES OF β,β' -DICHLORO-ETHYL SULFIDE.

BY OREGON B HELFRICH¹ AND E EMMET REID

Received March 5 1920

Introduction.

In view of the prominence into which β,β' -dichloro-ethyl sulfide has been recently brought by reason of its use in the war as "mustard gas," it was thought that an investigation of the chemistry of this substance would be of particular interest. While mustard gas on the battle field was the most permanent of the gases used in large quantity and was apparently inert, it has been found that it can take part in quite a variety of reactions. The purpose of this work² has been to make a study of certain of these reactions. The study has been limited to the reactions which involve the sulfur atom and the 2 chlorine atoms. Since the reactions involving the chlorine atoms always removed them, generally as sodium

¹ From dissertation of Oregon B Helfrich.

² The mustard gas used in this investigation consisted of crude material obtained from both the American University Experiment Station and the Edgewood Arsenal, and of some of the redistilled product from the first mentioned place. The crude material was used as a source of the dichloro-ethyl sulfoxide and sulfone while the redistilled product was used in the condensations.

chloride or hydrochloric acid, while those reactions involving the sulfur atom merely raised it to a higher state of oxidation, there exists in common among all the derivatives prepared what might be called the "mustard residue," $-\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2-$. The feasibility of giving this group a special name such as "mustarene" and calling its derivatives "mustarides," etc., was abandoned¹ in favor of names conforming with the system of nomenclature now being used in *Chemical Abstracts*.

Historical.

The only derivatives of this class that have previously been prepared, aside from the substances thiodiglycol,¹ $\text{S}(\text{CH}_2\text{CH}_2\text{OH})_2$, and ethylene disulfide,² $\text{S}(\text{CH}_2\text{CH}_2)_2\text{S}$, which have been known for a long time, are the 4-alkyl-1,4-thiazans which Clarke³ synthesized by the condensation of aliphatic amines with dichloro-ethyl sulfide, and the dichloro-ethyl sulfoxide and sulfone which were obtained during the war investigations.

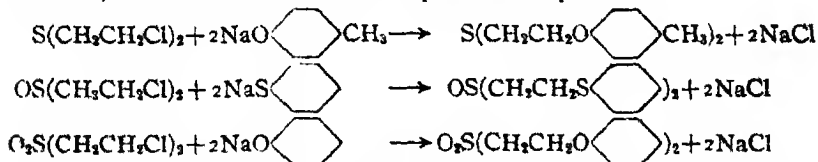
Outline of Present Study.

I. Products obtained by the oxidation of dichloro-ethyl sulfide

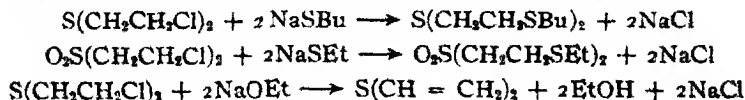


Dichloro-ethyl sulfide. Dichloro-ethyl sulfoxide Dichloro-ethyl sulfone.

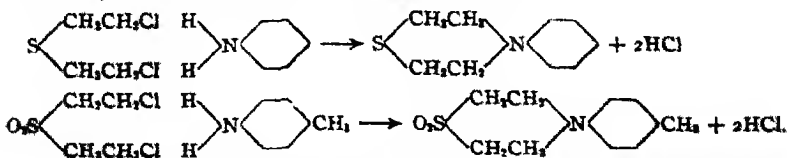
II. Products obtained by the condensation of dichloro-ethyl sulfide, sulfoxide, and sulfone with sodium thiophenate and phenates:



III. Products obtained by the reaction of dichloro-ethyl sulfide, sulfoxide, and sulfone with sodium mercaptides and alcoholates:



IV. Products obtained by the condensation of dichloro-ethyl sulfide, sulfoxide, and sulfone with the aromatic amines.⁴



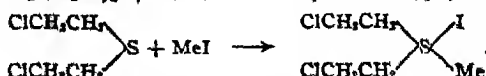
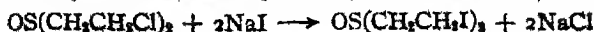
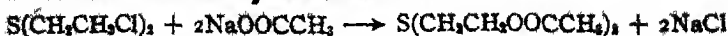
¹ Communication with Dr. E. J. Crane on this point led to the adoption of the names to be found in the following pages.

² V. Meyer, *Ber.*, 19, 3259 (1886); Crafts, *Ann.*, 124, 110 (1862).

³ *J. Chem. Soc.*, 101, 1583 (1912).

⁴ Similar to Clarke's synthesis of the 4-alkyl-1,4-thiazans.

V. Products obtained by other reactions.



In order to confirm the formulas of the derivatives prepared analyses were carried out in practically every case, usually the sulfur only being determined. The sulfur analyses were made by the sodium peroxide fusion, carried out in the Parr bomb,¹ with subsequent precipitation and determination of the sulfur as barium sulfate. This method was found very convenient and gave good results with all the crystalline derivatives, but with the few oily derivatives the results were hardly satisfactory, the analytical figures quoted in these cases being usually the best pair out of about 5 analyses. As the composition of these oils was rather definitely fixed by their method of preparation and by their oxidation products, little time was spent in the development of the method of analysis. In the few cases where analyses for halogen were made, the method used was to decompose the substance with sodium in absolute alcohol and then to determine the halogen, in the usual way, as silver halide.

I. Oxidation Products.

(a) β, β' -Dichloro-ethyl Sulfoxide, (bis(β -chloro-ethyl)Sulfoxide), $(ClCH_2CH_2)_2SO$.—In a report of war gas investigations there is a statement to the effect that dichloro-ethyl sulfide is oxidized by conc. nitric acid to the corresponding sulfoxide² melting at 109.5° . No further information regarding the preparation or the substance itself is vouchsafed. Since in the present work a detailed study of the substance has been made, the results are herein set forth.

When pure dichloro-ethyl sulfide is dropped into conc. nitric acid at room temperature, there is energetic reaction with evolution of heat and formation of a light green solution. From this solution, after diluting with water, the sulfoxide separates as white crystal plates. These melt constant at 109.5° (corr.) which agrees with the melting point given in the war gas report.

So far as one can judge by handling this substance it is entirely without effect upon the human skin.

Dichloro-ethyl sulfoxide is soluble in a variety of solvents, *e. g.*, water, conc. mineral acids (especially), alcohol, ether, benzene, carbon disulfide, and acetone. At 20° , 100 cc. of water dissolves 1.2 g. of sulfoxide; and

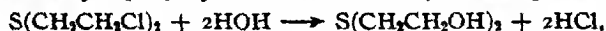
¹ *J. Ind. Eng. Chem.*, 11, 230 (1919).

² For brevity dichloro-ethyl sulfoxide will be referred to as the *sulfoxide* wherever clearness will permit.

at 100°, more than its own weight, in fact no limit could be found. At 20°, 100 cc. of alcohol¹ dissolves 4.3 g. of sulfoxide, at 80°, the solubility seems infinite. A large temperature coefficient of solubility is at once apparent for the sulfoxide in these 2 solvents. In conc. mineral acids the sulfoxide is quite soluble even at room temperature, due, no doubt, to the basic nature of the sulfoxide.

Dichloro-ethyl sulfoxide can not be distilled without partial decomposition even at reduced pressure. The chief decomposition product is dichloro-ethyl sulfide. No dichloro-ethyl sulfone can be detected in the distillate. It seems that during the distillation the sulfoxide dissociates into the sulfide and oxygen, the former appearing in the distillate and the latter either escaping as such or effecting a destructive oxidation of some of the sulfoxide.

Hydrolysis of the Sulfoxide.—Although dichloro-ethyl sulfide is hydrolyzed fairly rapidly by hot water according to the equation.



dichloro-ethyl sulfoxide is practically unchanged even in boiling water, the solution giving no precipitate with silver nitrate solution. The dichloro-ethyl sulfone in boiling water gives a precipitate of silver chloride with silver nitrate solution, thus showing a greater hydrolysis than the sulfoxide. Conductivity measurements also confirm the greater hydrolysis of the sulfone. Dichloro-ethyl sulfoxide is completely hydrolyzed by alcoholic sodium hydroxide, dihydroxyethyl sulfoxide $((HOCH_2CH_2)_2SO)$, a viscous oily liquid, easily soluble in water, alcohol, and ether, being obtained.

Reactions.—Dichloro-ethyl sulfoxide is oxidized by various reagents, best by chromic acid, to the corresponding sulfone which is described below. By virtue of the presence of the two halogen atoms, dichloro-ethyl sulfoxide is able to participate in many reactions analogously to the dichloro-ethyl sulfide. The derivatives so obtained will be considered in connection with the corresponding derivatives from the sulfide.

Experimental.

Preparation.—50 g. of pure dichloro-ethyl sulfide was dropped slowly into 100 g. of conc. nitric acid in a small balloon flask. The temperature was kept below 50 to 55° in order to avoid loss. After the addition was complete, the acid solution was filtered through asbestos (when the sulfide used was not pure there always separated considerable sulfur) and poured into 250 cc. water. Upon standing the sulfoxide came out as a beautiful white crystalline product. After several hours it was filtered with suction and the product dried. Yield, 80–85%. This was quite pure and generally melted about 106–7°. Recrystallization out of alcohol or water

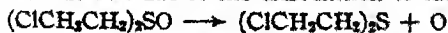
¹ Unless otherwise specified "alcohol" means the usual 95% material.

gave the pure substance, melting at 109.5° (corr.). When crude dichloro-ethyl sulfide was used, care had to be taken in the addition to the acid, as the reaction was considerably more violent. A sample of crude mustard gas from the American University gave on oxidation a light brown product (melting at $105^{\circ}\pm$) in about 55% yield. A sample of the crude material from the Edgewood Arsenal, of slightly better grade, gave an almost white product in about the same yield. The sulfoxide obtained from either source melted at 109.5° , after one recrystallization out of hot water. Sulfur analysis gave S; 18.50 and 18.26%, calc. 18.30%.

Distillation.—50 g. of dichloro-ethyl sulfoxide was distilled *in vacuo*. The distillate came over between 105 – 145° under 18 mm. pressure. It was composed of a white solid and 2 apparently immiscible liquids. Some of the white solid was separated and treated in alcohol solution with sodium thiophenate and the resulting product recrystallized out of alcohol to constant melting point. It melted at 121.0° showing it to be bis(β -phenyl-mercapto-ethyl) sulfoxide (described below) which proves that the white solid was unchanged dichloro-ethyl sulfoxide. The oily portion of the distillate was shaken with water, becoming in this operation one homogeneous oil, no doubt by solution of the other liquid (perhaps a water solution of the sulfoxide), then the oil separated and was distilled *in vacuo*. The main portion came over between 95° and 107° under 12 mm. pressure. This was further fractionated and came over nearly constant at 105 – 8° under 18 mm. pressure. As this boiling point was rather indicative of mustard gas, care was exercised in handling it. The distillate was a pale yellow oil of faint odor similar to that of mustard gas. On treatment in alcohol solution with sodium thiophenate and recrystallization of the product out of alcohol, it yielded bis(β -phenyl-mercapto-ethyl) sulfide melting at 57.5° . Together with the other data this clearly showed the main decomposition product during the distillation to have been dichloro-ethyl sulfide. After finding the sulfide as a product of decomposition it was thought probable that some sulfone might be present also if decomposition had taken place according to the reaction:



But no sulfone was found. Indeed the amount of actual sulfide isolated practically excluded any such possibility. It seems probable that the formation of the sulfide was due to the dissociation of the sulfoxide thus:



the oxygen being consumed in some oxidation-decomposition reaction.

Solubilities.—The sulfoxide was shaken with water and with alcohol for 2 days at 20° and assuming saturation at the end of that time, samples of the solutions were weighed (or measured), evaporated to dryness and the residues weighed.

Sulfoxide in water at 20°

Sample of Solution No 1 weighed 13.48 g — residue 0.15 g \approx 1.1 g. per 100 cc.

Sample of Solution No 2 weighed 11.09 g — residue 0.13 g \approx 1.2 g. per 100 cc.

Sulfoxide in alcohol at 20°.

Sample of Solution No 1, 10 cc — residue 0.42 g \approx 4.2 g per 100 cc.

Sample of Solution No 2, 10 cc — residue 0.44 g \approx 4.4 g per 100 cc.

Hydrolysis of the Sulfoxide.—I. Information furnished by treatment with silver nitrate as to the presence of the chlorine ion in the water solution of dichloro-ethyl sulfoxide

100 cc. of a boiling 1% solution of the sulfoxide gave no precipitate on the addition of 20 cc. of 5% silver nitrate solution. Hydrolysis must be very low.

On the other hand 100 cc. of a boiling 1% solution of the sulfone did give a definite precipitate of silver chloride on the addition of 20 cc. of a 5% silver nitrate solution. Whence hydrolysis is greater than with the sulfoxide.

II. Conductivity measurements relative to hydrolysis.

Dilute aqueous solutions of the sulfoxide and sulfone were made, their initial conductances measured and after 10 days the conductances again determined. It was found that at 20° there was no change in the conductance of the sulfoxide solution while, under identical conditions, the conductance of the sulfone solution increased about 20%. This clearly demonstrates the greater hydrolysis in the latter solution. Measurements were also made keeping the solutions at 100° but the results were worthless because a blank showed that the solubility of the glass in the tubes used was more than sufficient to produce the effects noted

III. Preparation of the hydrolysis product.

Fifteen g. of sulfoxide was added to a hot solution of 8 g. of sodium hydroxide in 100 cc. of alcohol. The separation of sodium chloride was rapid. Most of the alcohol was evaporated off on the steam bath, the product treated with water, and extracted with ether. The extract was separated off, dried, and evaporated, yielding the dihydroxyethyl sulfone as a light brown syrup. This was somewhat deliquescent and easily soluble in water, alcohol, and ether.

(b) Dichloro-ethyl Sulfone (Bis(β -chloro-ethyl)sulfone), $(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$.—When dichloro-ethyl sulfoxide is further oxidized by the use of fuming nitric acid, potassium permanganate, or chromic acid, the chief product is the corresponding sulfone.¹ When this step is carried out by a hot aqueous solution containing 5–10% chromic acid and 15–18% sulfuric acid the yield is nearly quantitative. By the use of the other 2 oxidizing agents the yield of sulfone is not so good since considerable amounts of the sulfoxide are either completely oxidized or converted into other products not easily isolated. In the report previously referred to,

¹ Whenever clearness permits, dichloro-ethyl sulfone will be called "the sulfone."

It was stated that dichloro-ethyl sulfone is obtained by oxidation with fuming nitric acid and that it melts at 54.0° . No further details were given. In the present study dichloro-ethyl sulfone has been studied in some detail, as was the sulfoxide, and is presented accordingly.

Dichloro-ethyl sulfone crystallizes out of alcohol or water in beautiful thin white leaflets melting at 56.0° (corr.), or 2° higher than figure given above. Upon distillation at atmospheric pressure it undergoes partial decomposition, boiling at about 230° , with evolution of hydrogen chloride and sulfur dioxide, yielding as distillate a yellow oil containing much unchanged sulfone and as residue a considerable amount of carbonized matter. Under 20 mm. pressure, however, it boils without decomposition at 183° the distillate solidifying easily and melting at $55-6^{\circ}$. The solubility of the sulfone in water and dil. acids is much less than that of the sulfoxide, probably because of the lack of the basic properties in the sulfone. At 20° 100 cc. of water dissolves 0.6 g. of sulfone, at 100° 2.4 g. When it is recalled that the sulfoxide is practically infinitely soluble in water at 100° the difference between these compounds in their relation toward water is at once apparent. In alcohol, which may be taken as representative of the organic solvents, the sulfone is slightly more soluble than the sulfoxide; at 20° , 100 cc. of alcohol dissolves 7.1 g. of sulfone and at 80° the solubility is very great.

Physiological Action of the Sulfone.¹—Dichloro-ethyl sulfone produces on contact with the skin blisters and persistent sores. Its vapors are lachrymatory, causing soreness of the eyes, and somewhat sternutatory, causing a slight burning in the nostrils, but as its vapor pressure is so low at ordinary temperatures that no inconvenience is experienced in handling it. That these unpleasant properties should reoccur in the sulfone after disappearing in the sulfoxide is peculiar. The theory² has been advanced that hydrolysis is one of the main factors entering into the action of dichloro-ethyl sulfide on the human body. It is of interest to note here that the hydrolysis of the sulfide by water is greatest, the sulfone next and the sulfoxide least. These facts are in accordance with the theory mentioned as applied to the observed physiological effects of the sulfoxide and sulfone.

Hydrolysis of the Sulfone.—In regard to the actual hydrolysis of the dichloro-ethyl sulfone the following calculation is of interest. A 1% solution of the sulfone in water at 100° gives a partial precipitation of its chlorine as silver chloride when treated with 20 cc. of 5% silver nitrate solution. The 5% silver nitrate solution = 0.3 M whence the concentration of AgNO_3 (= Ag^+) after addition to the 100 cc. of sulfone solution is 0.05 M. For calculation take the solubility of silver chloride at 100°

¹ Unpublished report of Dr. E. K. Marshall.

² E. K. Marshall, *J. Am. Med. Assoc.*, 73, 684 (1919); *C. A.*, 13, 2929 (1919).

$= 1.0 \times 10^{-4}$. That is $K_{AgCl} = 1.0 \times 10^{-10}$. Since there was some precipitation of silver chloride, we know that $(Ag^+ \times Cl^-) = K_{AgCl}$ or $(0.05) \times (Cl^-) = 1.0 \times 10^{-10}$. That is $Cl^- > 2.0 \times 10^{-9}$ in the boiling sulfone solution. Since, however, precipitation is incomplete we know further that the Cl^- concentration only exceeded the value 2.0×10^{-9} by a small amount. These figures give a fair idea of the hydrolysis of the sulfone in boiling water. In cold water it is, of course, much less, as no precipitate of silver chloride is obtained in the cold. It is regretted that time was not available to make a more exact study of these relations.

β,β' -Dihydroxy-ethyl sulfone is prepared by the hydrolysis of the dichloro-ethyl sulfone by alcoholic sodium hydroxide. It is a thick syrup, somewhat deliquescent, and in general similar to the sulfoxide analogue. It is difficult to obtain entirely free from water. The best product obtained boiled under 15 mm. pressure evenly distributed over the range $140-165^\circ$.

Reactions.—When an alcohol solution of dichloro-ethyl sulfone is treated with an alcohol solution of sodium sulfide, reaction is very rapid. The product is an amorphous white solid (probably $S < (CH_2CH_2)_2 > SO_2$), which does not melt at 200° , and is insoluble in the ordinary solvents.

The other products obtained from the sulfone by the replacement of its chlorine atoms will be taken up in connection with the similar derivatives of dichloro-ethyl sulfide.

Experimental.

Preparation.—50 g. of dichloro-ethyl sulfoxide was heated in 350 cc. of water, containing 25 g. of chromic acid (or the equivalent amount of sodium dichromate) and 40 cc. of conc. sulfuric acid, for a period of 4 to 6 hours. The reaction mixture was then allowed to cool and to stand several hours before filtering. The crude product as filtered off was quite dark from chromium salts and was digested with 100 cc. of boiling water. After the sulfone had solidified by cooling the water was poured off and the product dissolved in 100 cc. of hot alcohol. The solution was filtered hot and after cooling the white, or pale-greenish, product filtered off and dried. A second crop of good material was obtained by adding an equal volume of water to the alcohol mother liquor. Yield, 50 g.; m. p., $55-6^\circ$. On recrystallization the pure substance melted at 56.0° .

Distillation.—100 g. of sulfone distilled at ordinary pressure at about 230° with considerable decomposition, yielding a clear yellow oil as distillate, while giving off hydrogen chloride and sulfur dioxide. About $\frac{1}{2}$ of the original material remained in the distilling bulb as a carbonized residue. The yellow oil distilled over again at 230° with evolution of more hydrogen chloride and sulfur dioxide. Again there was a carbonized residue. The distillate now weighed 35 g. Determination of the chlorine content showed 14.5%, a proportion which did not indicate any simple

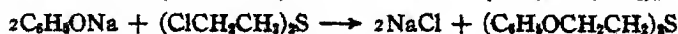
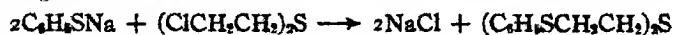
Decomposition product. $(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$ contains 36.6%, $\begin{array}{c} \text{ClCH}_2\text{CH}_2 \\ | \\ \text{CH}_2\text{CH}_2 \end{array} \text{SO}_2$

contains 22.9%. A sample of the oil treated with sodium thiophenate in hot alcohol solution gave a separation of sodium chloride and, on diluting with water, an oily crystal pulp was obtained. By recrystallization out of alcohol crystals melting at 104.5° were isolated. This melting point corresponds exactly with that of bis(β -phenyl-mercapto-ethyl) sulfone, obtained by the condensation of sodium thiophenate with dichloro-ethyl sulfone. Thus it appears that there was some unchanged sulfone still in the oil after 2 distillations at atmospheric pressure. From the chlorine content it seems that the oil in question contained about 40% of the sulfone dissolved in some oily chlorine-free sulfur compound. The nature of the oily constituent was not determined. The fact that the decomposition took place practically constantly at 230° should be noted. When the final yellow oil was distilled *in vacuo* there was practically no decomposition but the distillation took place over quite a range of temperature ($\frac{2}{3}$ of the total came over between 125 – 150° under 23 mm. pressure), showing clearly that this oil was not a single substance, as the constant boiling point (with decomposition) at atmospheric pressure might have led one to believe.

The pure dichloro-ethyl sulfone distills *in vacuo* without any decomposition at 183° under 20 mm. pressure.

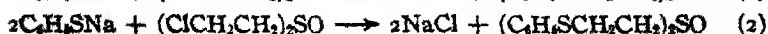
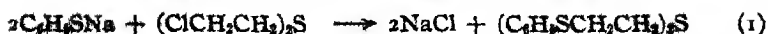
II. Products by Condensation with Sodium Thiophenate and Phenates.

The fundamental reaction in the preparation of these derivatives is the formation of sodium chloride with the simultaneous condensation of the organic residues.



It is seen that the condensation with sodium thiophenate gives complex trisulfides or related bodies, while with the phenates it produces various mixed sulfide-ethers. All of these substances which have been prepared are white (or nearly so) crystalline bodies. Most of them can be recrystallized out of alcohol but those from the more complex phenols (α - and β -naphthol, eugenol, vanillin, tribromo-phenol) are only slightly soluble. None of the derivatives is soluble in water. So far as has been ascertained none of them is dangerous to work with. The yields in general are good. For those products obtained from sodium thiophenate the yields are nearly quantitative.

The stability of the multiple-sulfides and their oxidation products, together with the quantitative nature of the condensation of sodium thiophenate with dichloro-ethyl sulfide, -sulfoxide, or -sulfone are among the outstanding features of this field. While the reactions



with thiophenate all take place nearly quantitatively, the corresponding ones with sodium phenate give smaller and varying yields. Thus the reaction corresponding to (1) gives a good yield, the reaction corresponding to (2) gives none of the desired product, while the reaction corresponding to (3) gives the expected product but only in poor yield. These relations hold in general also for the other phenols which condense readily with only the dichloro-ethyl sulfide. With regard to oxidation the sulfide-ethers function entirely differently from the multiple-sulfides. Thus it has been found that the former are entirely broken down by nitric or chromic acid (giving in several cases quinone), while in the latter the sulfur atoms alone are oxidized to the quadrivalent or hexavalent condition, the chain of sulfur and carbon atoms remaining unbroken. In general nitric acid oxidizes the sulfide groups to sulfoxide groups, while chromic acid or permanganate oxidizes either of these to sulfone groups.

A systematic study of the oxidation products of bis(β -phenyl-mercapto-ethyl) sulfide, $(\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2)_2\text{S}$, has been made and the following series developed:

Name (Formula)	Sulfur		M p (corr) °C	Sol in 100 cc Alc		Remarks.
	Calc.	Found		Cold (18° ±)	Hot (75° ±)	
Bis(β -phenyl mercapto-ethyl) sulfide $(\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2)_2\text{S}$	31.40	31.66 31.43	57.50	65 g	10 g	Lustrous white leaflets
Bis(β -phenyl-mercapto-ethyl) sulfoxide $(\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2)_2\text{SO}$	29.81	29.98 29.67	121.01	0 g	sol	Lustrous white leaflets
Bis(β -phenyl-sulfinyl-ethyl) sulfoxide $(\text{C}_6\text{H}_5\text{SOCH}_2\text{CH}_2)_2\text{SO}$	27.12	26.90 27.04	161.05	sol	sol	Small white crystals
Bis(β -phenyl-mercapto-ethyl)sulfone $(\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2)_2\text{SO}_2$	28.40	28.40 28.27	104.55	sol	sol	Lustrous white leaflets
Bis(β -phenyl-sulfinyl-ethyl)sulfone $(\text{C}_6\text{H}_5\text{SOCH}_2\text{CH}_2)_2\text{SO}_2$	25.95	25.84 26.07	164.0	insol	sol	Small white plates
Bis(β -phenyl-sulfonyl-ethyl)sulfone $(\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2)_2\text{SO}_2$	23.83	23.80 23.74	235.0	insol	insol	White needles

Attention is here called to the fact that these oxidation products of the multiple-sulfides should furnish excellent material for a study of the relation between certain physical properties, especially melting points and solubilities, and the chemical composition and structure. These compounds form a series of closely related derivatives, differing only by slight degrees of oxidation of the sulfur atoms and not by any changes in the

main skeleton. Consideration of the table shows what a large influence the oxidation of the sulfur atoms has upon the melting point in these trisulfides. The stabilizing influence of raising the sulfur atom to its higher valences is therein apparent. When one considers that in a molecule containing bivalent sulfur atoms there must exist in consequence of the higher valence possibilities of the sulfur atom not only reactive tendencies toward certain classes of substances but also within the molecule itself a certain flexibility of structure, it is easy to conceive that the oxidation (*i. e.*, saturation) of these sulfur atoms should exert a large influence on the rigidity of the structure of the molecule and thereby effect the melting point and other properties. That the trisulfone which contains completely saturated sulfur atoms should be at the top of the series with regard to melting point, difficulty of solution in organic solvents, etc., is at once obvious.

Such reasoning apparently fails in the case of the simpler series but it




$(\text{ClCH}_2\text{CH}_2)_3\text{S}$	$\text{Cl}(\text{CH}_2\text{CH}_2)_3\text{SO}$	$\text{Cl}(\text{CH}_2\text{CH}_2)_3\text{SO}_2$
14 4°	109 5°	56 0°

should be recalled that the present work has already pointed out that dichloro-ethyl sulfoxide lies out of line with the sulfide and sulfone in physiological properties and in hydrolysis. It is probable that there is a specific effect exerted by the presence of the sulfoxide group together with 2 chlorine atoms in the β -positions. Any such specific effect would of course prevent the successful application of the above reasoning with regard to physical properties.

Condensation with Phenols.—The sulfide-ethers, already referred to, now come up for specific discussion. Since the condensation between the phenates and dichloro-ethyl sulfoxide does not take place at all, and with dichloro-ethyl sulfone the yield is rather poor, most of the derivatives prepared are of the structure $(\text{ROCH}_2\text{CH}_2)_2\text{S}$ where "R" is an aromatic residue. Further, since these sulfide-ethers are unstable towards oxidation it has been impossible to complete the series of oxidation products.

The sulfide-ethers and sulfone-ethers are nicely crystallized substances, insoluble in water, the simpler ones easily soluble in hot alcohol, the more complex ones rather difficultly. So far as known they have no effect on the human skin.

A number of aromatic phenols was tried unsuccessfully in this work. Those which failed to give the condensation were *p*-chlorophenol, *p*-nitrophenol, thymol, resorcin, methyl salicylate, and ethyl salicylate. No explanation for the discrepancy in the action of the phenol group in these compounds has been developed. In these cases where the condensation does not take place the sodium hydroxide present hydrolyzes the dichloro-ethyl sulfide with separation of sodium chloride from the alcohol solution

Name. (Formula)	Sulfur		M p (Corr) °C	Sol in 100 cc. Alc.		Remarks
	Calc	Found		Cold (18 0)	Hot (75 0)	
Bis(β -phenoxy-ethyl) sulfide (C ₆ H ₅ OCH ₂ CH ₂) ₂ S	11 68	11 67 11 70	54 2	1 4 g	20 g	Fine white needles
Bis(β -phenoxy-ethyl) sulfone (C ₆ H ₅ OCH ₂ CH ₂) ₂ SO ₂	10 46	10 30 10 41	108 0	s sol	sol	Pinkish leaflets
Bis(β - <i>p</i> -cresoxy-ethyl) sulfide (<i>p</i> -CH ₃ C ₆ H ₄ OCH ₂ CH ₂) ₂ S	10 60	10 55 10 68	78 0	0 2 g	sol	Lustrous needles
Bis(β - <i>p</i> -cresoxy-ethyl) sulfone (<i>p</i> -CH ₃ C ₆ H ₄ OCH ₂ CH ₂) ₂ SO ₂	9 58	9 64 9 58	120 0	s sol	sol	Small pink leaflets
Bis(β - <i>o</i> -cresoxy-ethyl) sulfide (<i>o</i> -CH ₃ C ₆ H ₄ OCH ₂ CH ₂) ₂ S	10 60	10 47 10 51	46 5	0 3 g ^a	sol	White needles
Bis(β - α naphthoxy-ethyl) sulfide (α -C ₁₀ H ₇ OCH ₂ CH ₂) ₂ S	8 55	8 60 8 46	94 5	insol	s sol	Light brown crystals
Bis(β - β -naphthoxy-ethyl) sulfide (β -C ₁₀ H ₇ OCH ₂ CH ₂) ₂ S	9 55	8 48 8 51	129 0	insol	0 6 g	Small crystals
Bis(β - β -naphthoxy-ethyl) sulfone (β -C ₁₀ H ₇ OCH ₂ CH ₂) ₂ SO ₂	7 88	7 90 7 76	151 0	s sol	sol	Small shining plates
Bis(β -vanilloxy-ethyl) sulfide (HOC-  OCH ₂ CH ₂) ₂ S	8 25	8 22 8 24	131 5	insol	2 g	Gray needles
Bis(β -eugenoxo-ethyl) sulfide (CH ₃ CHCH ₂ -  OCH ₂ CH ₂) ₂ S	7 73	7 80	113 5	0 1 g	2 g	Yellow powder
Bis(β -tribromo-phenoxy-ethyl) sulfide (Br-  OCH ₂ CH ₂) ₂ S	4 29	4 29 4 26	118 5	insol	0 5 g	White powder

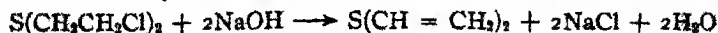
^a Solubility in 70% alcohol

as usual, the reaction going for the most part according to the equation



This hydrolysis takes place to some extent also even in the cases where the condensation takes place but it is exceeded by the more rapid condensation. In the case of the thiophenol condensation the hydrolysis reaction is entirely negligible on account of the rapidity of the condensation. It is probable that both reactions go on simultaneously, their relative velocities depending on the properties of the reactants.

Another reaction which probably takes place to some extent is the formation of vinyl sulfide. If dichloro-ethyl sulfide is treated with



sodium ethylate, vinyl sulfide seems the main product. The slow hydrolysis of dichloro-ethyl sulfide by alkali in 50% alcohol in the cold gives

a rather high-boiling oil, insoluble in water and heavier than water. This is certainly not thiodiglycol and from its odor and properties may be a polymer of vinyl sulfide. Investigation of this point was cut short by an accident.

Experimental.

It would be useless repetition to give in detail the preparation of each of these derivatives. With the exception of the 3 products obtained by oxidation, which will be considered briefly below, they were all prepared by the following procedure.

0.01 Mole of dichloro-ethyl sulfide (-sulfoxide, or -sulfone) was added to a solution of 0.02 mole of the phenol (or thiophenol) in 20 cc. of *N* alcoholic sodium hydroxide, plus 25 cc. of alcohol and heated on the steam bath one hour. Then 20 cc. of water was added to dissolve the sodium chloride and cause the separation of the product, if this had not already taken place. The product was then filtered off and recrystallized to constant melting point and analyzed. The solubility figures given in the table are based on the weights of the crystals crop in successive recrystallizations. The figures thus make no claim for exactness yet give a fair idea of the solubility.

An example of the calculation of solubility is given.

Bis(β -phenyl-mercapto-ethyl) sulfide recrystallized from 50 cc portions of alcohol

{	1st 1st, m p. 57°	wt 3.91 g	1st 2nd, oil
	2nd 1st, m p 57.5°	wt 3.63 g	2nd 2nd, m p 57°
	3rd 1st, m p 57.5°	wt 3.28 g	3rd 2nd, m. p. 57.5°

The difference in weight between the 1st 1st and 2nd 1st is 0.28 g., and between the 2nd 1st and 3rd 1st is 0.35 g. The average is 0.32 g. and assuming this to represent the amount dissolved in the 50 cc. alcohol at the temperature of filtration (18°), we find 0.65 g. per 100 cc. as an estimate of the solubility at that temperature. In those cases where the solubility in cold alcohol was extremely low, there has been given as an estimate of the solubility at 75° the weight of the substance separating on cooling from 100 cc. alcohol which had been boiled with an excess of the substance and then very rapidly filtered while boiling hot.

Oxidation of Products.—The preparation of the 3 products obtained by oxidation methods will now be given.

1. Bis(β -phenyl-sulfinyl-ethyl) sulfoxide ((PhSOCH₂CH₂)₂SO) was prepared by the oxidation of bis(β -phenyl-mercapto-ethyl) sulfide ((PhSCH₂CH₂)₂S) by conc. nitric acid. The preparation was difficult and the yield poor. Nitric acid was added very slowly drop by drop to the sulfide until the first energetic reaction was over and the oil barely dissolved to form a clear yellow solution. On diluting a yellowish white product separated in small amount and was recrystallized out of alcohol. If an excess of nitric is used no crystal product is obtained.

2. Bis(β -phenyl-sulfinyl-ethyl) sulfone ((PhSOCH₂CH₂)₂SO₂) was

prepared similarly by the oxidation of bis(β -phenyl-mercapto-ethyl) sulfone $((\text{PhSCH}_2\text{CH}_2)_2\text{SO}_2)$ by nitric acid. The preparation in this case was not difficult and the yield satisfactory. On account of its low solubility even in boiling alcohol the product was recrystallized from nitric acid.

3. Bis(β -phenyl-sulfonyl-ethyl) sulfone $((\text{PhSO}_2\text{CH}_2\text{CH}_2)_2\text{SO}_2)$ was prepared by the oxidation of any of the lower oxidized substances of the same skeleton by either permanganate or chromic acid. The product was recrystallized out of nitric acid, being practically insoluble in alcohol.

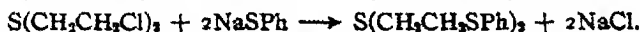
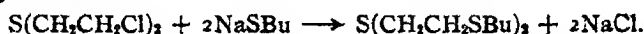
(a) Three g. of bis(β phenyl-mercapto-ethyl) sulfide (or sulfone, etc.), was heated in a solution of 5 g. of chromic acid and 10 cc of conc. sulfuric acid in 100 cc of water for $1\frac{1}{2}$ hour on a steam bath. After cooling the crude product was filtered off.

(b) Three g of bis(β -phenyl-mercapto-ethyl) sulfide (or sulfone, etc.), was dissolved in 10 cc. of conc. nitric acid, 100 cc. water added, and the boiling acid solution treated with potassium permanganate solution as long as the latter was decolorized and the white precipitate of the product continued to form. The crude product was filtered off.

The purified products were identical.

III. Products by Condensation with Sodium Mercaptides (and Alcohates).

The condensation of dichloro-ethyl sulfide (-sulfoxide, or -sulfone) with sodium mercaptides is quite similar to that with sodium thiophenolate already considered.



The reaction is rapid in the hot alcohol solution and the yields nearly quantitative. The stability of these multiple-sulfides and their oxidation products is again an outstanding feature.

(Formula)	Sulfur		B. P.	M. P. (corr.)	Remarks.
	Calc.	Found			
Bis(β -butyl-mercapto-ethyl) sulfide $(\text{BuSCH}_2\text{CH}_2)_2\text{S}$	36.09	35.53 35.31	222-3	17.5	Oil, unpleasant persistent odor
Bis(β -butyl-mercapto-ethyl) sulfoxide $(\text{BuSCH}_2\text{CH}_2)_2\text{SO}$	34.04	"	.	25.0	Oil, very slight odor
Bis(β -butyl-sulfinyl-ethyl) sulfoxide $(\text{BuSOCH}_2\text{CH}_2)_2\text{SO}$	30.57	30.36 30.42		196.0	Brilliant small white crystals
Bis(β -butyl-mercapto-ethyl) sulfone $(\text{BuSCH}_2\text{CH}_2)_2\text{SO}_2$	32.21	32.10 32.14		73.7	Shining white needles
Bis(β -butyl-sulfinyl-ethyl) sulfone $(\text{BuSOCH}_2\text{CH}_2)_2\text{SO}_2$	29.09	29.05 28.98		101.0	Very small gray-white crystals
Bis(β -butyl-sulfonyl-ethyl) sulfone $(\text{BuSO}_2\text{CH}_2\text{CH}_2)_2\text{SO}_2$	26.52	26.36 26.52		266.5	Glittering gray crystal plates

* Analysis not run on account of nature and small quantity of material.

From the condensation products obtained by the use of butyl mercaptan a series of oxidation products has been prepared analogous to that obtained from the thiophenol derivatives.

Just as with the similar phenyl derivatives the last 2 compounds of the table are only slightly soluble in organic solvents. For purification it is necessary to recrystallize bis(β -butyl-sulfonyl-ethyl) sulfone out of nitric acid; bis(β -butyl-sulfinyl-ethyl) sulfone may be recrystallized out of either alcohol or nitric acid. In general these butyl derivatives are slightly more soluble than the corresponding phenyl derivatives. In this (butyl) series the trisulfoxide (bis(β -butyl-sulfinyl-ethyl) sulfoxide) is prepared with greater ease though the yield is still poor. On comparing the melting points of the compounds it is seen that the trisulfoxide, trisulfone, and disulfoxide-sulfone of the butyl series melt higher than those of the phenyl series, while the other 3 members of the butyl series melt lower. This is a rather interesting point because it indicates that the oxidation of all 3 sulfur atoms in the butyl compounds must cause a considerably greater internal disturbance and rearrangement (in the direction of rendering the molecule more rigid in structure) than in the case of the phenyl compounds.

From the alkyl mercaptans lower than butyl such complete series have not been prepared. Various attempts to prepare the derivatives containing 2 and 3 sulfoxide groups have failed. The oxidation of the lower alkyl trisulfides with nitric acid neither breaks down the carbon-sulfur chain nor furnishes the desired sulfoxide. Thus bis(β -ethyl-mercapto-ethyl) sulfide, on oxidation with conc. nitric acid and subsequent dilution, furnishes no crystals of the trisulfoxide. However, the original skeleton has not been destroyed, for the addition of potassium permanganate to the nitric acid gives in fair yield the trisulfone (bis(β -ethyl-sulfonyl-ethyl) sulfone) which can be easily isolated.

The derivatives which have been prepared and investigated are contained in the following table. As might be surmised from what has just preceded, these fall into 3 classes (the sulfoxide types being missing), of which bis(β -butyl-mercapto-ethyl) sulfide and -sulfone and bis(β -butyl-sulfonyl-ethyl) sulfone are typical. The table is divided horizontally into 3 sections, one for each type of derivatives. The derivative in the first section (trisulfides) are all oils, freezing at about room temperature, immiscible in water, but soluble in the ordinary organic solvents. The members of the second section (disulfide-sulfones) are with one exception crystalline substances of sharp melting point, very slightly soluble in hot water, somewhat more so in hot dilute nitric acid, and easily soluble in hot alcohol. The members of the third section (di-sulfones) are high melting substances, insoluble in water and nearly so in alcohol, but easily crystallized from hot nitric acid. In the case of isobutyl-, secondary

butyl-, and amyl mercaptans, the supply on hand was so small that no attempt was made to develop the full series possible with them.

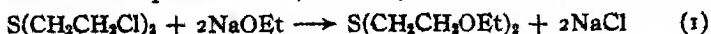
Name (Formula.)	Sulfur		β °C	β' °C	M.P. (corr) °C	Remarks.
	Calc	Found				
Bis(β -ethyl-mercapto-ethyl) sulfide (EtSCH ₂ CH ₂) ₂ S	45 71	45 43 45 31	173-5		17 0 $n_D^{22} = 1.5150$, odor rather unpleasant, and persistent	
Bis(β -propyl-mercapto-ethyl) sulfide (PrSCH ₂ CH ₂) ₂ S	40 33	40 12 19 96	193-5		27 5	
Bis(β -butyl-mercapto-ethyl) sulfide. (BuSCH ₂ CH ₂) ₂ S	36 09	35 53 35 31	222-3		17 5 $d_4^{20} = 1.02$, $n_D^{22} =$ 1.5455	
Bis(β -amyl-mercapto-ethyl) sulfide (i-AmSCH ₂ CH ₂) ₂ S	32 65	32 41 32 01	170		20 0	
Bis(β -methyl-mercapto-ethyl) sulfone (MeSCH ₂ CH ₂) ₂ SO ₂	44 86	44 59 44 61			77 0	Brilliant white leaflets
Bis(β -ethyl-mercapto-ethyl) sulfone (EtSCH ₂ CH ₂) ₂ SO ₂	39 67	39 51 39 44			64 0	Long thin white plates
Bis(β -propyl-mercapto-ethyl) sulfone (PrSCH ₂ CH ₂) ₂ SO ₂	35 55	35 51 35 44			75 5	Thin white waxy plates
Bis(β -butyl-mercapto-ethyl) sulfone (BuSCH ₂ CH ₂) ₂ SO ₂	32 31	32 10 32 14			73 7	Shining white needles
Bis(β -i-butyl-mercapto-ethyl) sul- fone. (i-BuSCH ₂ CH ₂) ₂ SO ₂	32 21	32 20 32 11			94 2	Shining white needles (broader)
Bis(β - (sec)butyl- mercapto-ethyl) sulfone ((sec)BuSCH ₂ CH ₂) ₂ SO ₂	32 21	32 18 32 07			15 0	Oil
Bis(β -amyl-mercapto-ethyl) sulfone (i-AmSCH ₂ CH ₂) ₂ SO ₂	29 45	29 33 29 51			91 0	Small white needles
Bis(β -ethyl-sulfonyl-ethyl) sulfone (EtSO ₂ CH ₂ CH ₂) ₂ SO ₂	31 17	31 21 31 29			223 0	Shining small thin white plates
Bis(β -propyl-sulfonyl-ethyl) sulfone (PrSO ₂ CH ₂ CH ₂) ₂ SO ₂	28 73	28 70 28 62			254 0	Thin white plates
Bis(β -butyl-sulfonyl-ethyl) sulfone (BuSO ₂ CH ₂ CH ₂) ₂ SO ₂	26 52	26 52			266 5	Very small white (gray) plates

The normal butyl derivatives are repeated for comparison.

A consideration of the table brings out several interesting points with regard to the melting points of these substances. Among the trisulfides the propyl derivatives stands out by reason of its melting higher than any of the others (ethyl-, butyl-, isoamyl-). Among the disulfide-sulfones the derivatives from the normal mercaptans show a definite alternation in their melting points, resembling the series with aliphatic acids, glycol, and amines. The derivatives from mercaptans containing an odd number of carbon atoms melt higher than the adjacent derivatives from mercaptans of even number of carbon atoms. Thus the methyl-derivative melts higher than the ethyl- while the propyl-derivative melts higher than all the normal derivatives below isoamyl-. The effect of the position of the carbon atoms is strikingly brought out in the butyl derivatives.

The *n*-butyl compound melts at 73.7°, the isobutyl- at 94.2°, and the secondary-butyl- at 15.0°.

Reaction with Alcoholates.—The reaction between dichloro-ethyl sulfide and sodium alcoholates now comes under consideration. Just as the phenols gave products similar to those obtained with thiophenol it was expected that the alcoholates would furnish derivatives similar to those of the mercaptides. Such, however, is not the case. The reaction



does not take place, or if it does the product indicated undergoes rapid decomposition. It seems that the chief product of the reaction is vinyl sulfide. This is easily understood, for alcoholic caustic soda frequently eliminates hydrochloric acid from aliphatic-halogen compounds forming unsaturated derivatives. The reaction here would be:



It might be considered that the mechanism of the reaction is bettered by a combination of (1) with the reaction



Experimental.

The trisulfides were prepared by adding 0.1 mole of dichloro-ethyl sulfide to an absolute alcohol (it was later found that 95% alcohol and sodium hydroxide acted as well) solution of 0.2 mole of sodium mercaptide, prepared by dropping 0.25 atom of sodium into 100 cc. of absolute alcohol and then adding 0.2 mole of mercaptan. The reaction mixture was warmed on a steam bath under a reflux condenser for 1/2 hour to cause the separation of sodium chloride, and then poured out into water. The product separated as an oil sinking to the bottom. The oil was separated, dried and distilled *in vacuo*. The yield was very good when pure mercaptans were used. Considerable difficulty was encountered in obtaining the pure isoamyl derivative because, as later found out, the original mercaptan (Kahlbaum's) was less than 70% pure, introducing considerable impurities difficult to separate. The distillation of these oils *in vacuo* proceeded very smoothly, no bumping or decomposition being observed.

The disulfide-sulfones were obtained in an analogous fashion from dichloro-ethyl sulfone and the mercaptides. These substances all separated as crystalline bodies on pouring the reaction mixture into water and were then recrystallized to constant melting point out of alcohol. Their solubilities in cold alcohol (18°) ranged from 1 to 4 g. while in hot alcohol they were all quite soluble.

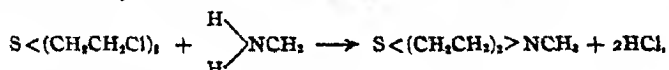
The preparation of the other compounds discussed was exactly analogous to the methods outlined for the corresponding phenyl derivatives.

Reaction with Alcoholates.—In the reaction between dichloro-ethyl

sulfide and the sodium alcoholates the product was apparently the same independent of nature of the alcoholate used. The reaction gave a separation of sodium chloride from the alcohol solution just as usual but the oil obtained on pouring into water was low boiling and had an odor resembling that described for vinyl sulfide. An unpurified lot of the oil distilled over at 60–70° with polymerization. Vinyl sulfide¹ boils at 102° but the lot distilled, no doubt, contained water and this together with the recognized abnormally high vapor pressures of vinyl sulfide at temperatures down towards room temperature could easily cause distillation at 60–70°. The products continually polymerized on redistillation and could not be obtained pure. This polymerization of vinyl sulfide has been previously observed.¹

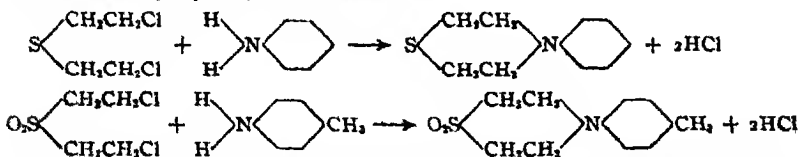
IV. Products by Condensation with Aromatic Amines.

Attention has already been called to the preparation by Clarke of several of the 4-alkyl-1,4-thiazans by the condensation of aliphatic amines with dichloro-ethyl sulfides. In his work the condensation



was carried out in absolute alcohol in the presence of dry sodium acetate at 100° (sealed tube).

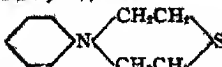
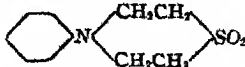
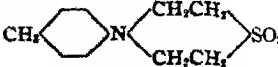
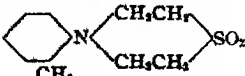
In the present investigation the *aromatic amines* have been condensed with dichloro-ethyl sulfide and sulfone, yielding respectively 4-aryl-1,4-thiazans and 4-aryl-1,4-sulfonazans



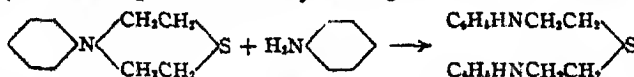
The sulfonazans are especially easy to prepare and work with. Thus, refluxing dichloro-ethyl sulfone with the desired amine in absolute alcohol solution in the presence of anhydrous sodium acetate gives the condensation readily. The thiazans can not be made thus. However, if dichloro-ethyl sulfide and aniline are mixed in the proper proportions and allowed to stand overnight the liquid becomes a mass of light brown crystals. From such a product the 4-phenyl-1,4-thiazan can be obtained in fairly pure condition. The sulfonazans are more easily prepared in a similar way, i. e., dichloro-ethyl sulfone and aniline (or other aromatic amine) are heated to 130°, the condensation being then quite rapid, and from the cooled product the pure 4-phenyl-1,4-sulfonazan is obtained by recrystallization out of alcohol or dil. hydrochloric acid.

¹ Semmler, *Ann.*, 247, 92 (1887).

THE DERIVATIVES PREPARED.

Name. (Formula)	Sulfur		M. p. (corr) °C	Remarks
	Calc	Found		
4-Phenyl-1,4-thiazan 	17 87	16 58 16 40	108-111	Dull white product, not pure Sol in hot toluene
4-Phenyl-1,4-sulfonazan . . . 	15 16	14 97 15 09	123 5	Clear gran crystals
4-p-Cresyl-1,4-sulfonazan . . . 	14 22	14 18 14 06	136 5	White plates out of aq. HCl Small gran crystals from alcohol
4-o-Cresyl-1,4-sulfonazan . . . 	14 22	14 31 14 12	135 0	Fernlike crystal aggregates out of alcohol

Only one of the 4-aryl-1,4-thiazans was prepared because of the difficulty of obtaining these derivatives. The difficulty encountered was based on 2 facts, (1) their insolubility (causing inconvenience in purification), and (2) their secondary reaction with excess aromatic amine, apparently to break open the heterocyclic ring



The compound resulting from the secondary reaction is easily soluble in dil. hydrochloric acid (quite in contrast with the thiazan), yielding in alkaline solution an oil heavier than water, which is only slightly volatile in steam. The composition of this substance has not been determined but there seems little reason to doubt that it is of the nature indicated in the equation.

The only method that has been found to yield the phenyl thiazan is to let the aniline and dichloro-ethyl sulfide mixture stand several days. Actually 2 moles of aniline are used for one mole of dichloro-ethyl sulfide in order that the liberated hydrochloric acid may be taken care of. Thus there is present one mole of excess aniline, and care must be exercised in order that the secondary reaction does not gain headway. The secondary reaction goes to completion if the reaction product is heated on the steam bath, giving an amber-colored clear solid (when cold) which dissolves completely in hot water. In the cold, however, the secondary reaction is negligible and the aniline hydrochloride may be leached out by water without harming a product which has been allowed to condense for several days at room temperature.

Dichloro-ethyl sulfide heated with 2 moles of *o*- or *p*-toluidine also gives water-soluble products. The reaction in the cold has not been studied.

In the condensation to form the sulfonazans the secondary reaction is not so important. Thus condensation at 130° gives 4-phenyl-1,4-sulfonazan in about 50% yield. It is, however, hardly to be doubted that some of reactants here also take part in a similar secondary reaction. Several attempts to prepare the sulfonazans from α - and β -amino-anthraquinone failed completely.

The alkyl thiazans prepared by Clarke are basic compounds of which the hydrochlorides and picrates are easily obtained. The lower members are very strong bases, very soluble in water and organic solvents and fuming in the presence of acids. The properties of the 4-phenyl-1,4-thiazan present a sharp contrast. It is insoluble in water and most organic solvents and its basic tendencies are almost negligible, it being only slightly soluble in hot hydrochloric acid.

The aryl sulfonazans present an interesting class of substances. They are easily obtained by the method outlined in this paper but can not be obtained by the oxidation of the aryl thiazans as one might conjecture from a comparison of the formulae. Not only from the point of view of a new heterocyclic type but also regarded as another group of tertiary aromatic amines they abound with possibilities. It is hoped that work may soon be carried out to ascertain their adaptability to the various condensations effected with the ordinary tertiary aromatic amines. Particular reference is had to the condensations resulting in the production of various dyes, *i. e.*, malachite green, crystal violet, etc.

Experimental.

Preparation of (4)-Phenyl-(1,4)-thiazan.—50 g. of dichloro-ethyl sulfide was mixed with 60 g. of aniline and let stand 3 days or more (solidification took place overnight). The brown crystal mass was leached twice with boiling water and once with very dilute hydrochloric acid to remove the last of the aniline. The residue was dissolved in hot 10% hydrochloric acid and poured into a large volume of cold water. The product separated first as gummy drops but on boiling the water these became completely solid. This grayish white product was filtered off, leached 3 times with 100 cc. portions of boiling alcohol and finally recrystallized from toluene. Even then it did not give a sharp melting point ($108-111^{\circ}$) showing the purification to be still incomplete.

Preparation of the (4)-Aryl-(1,4)-sulfonazans.—0.2 mole of aromatic amine was mixed with 0.1 mole of dichloro-ethyl sulfone and heated to 130° for 10-15 minutes. The condensation was rapid with resultant solidification of the product. This was dissolved in conc. sulfuric acid and poured into water. The crude crystal product separated and was re-

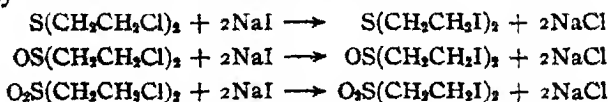
crystallized out of alcohol or dil. hydrochloric acid to constant melting point.

V. Products by Other Reactions.

In this section, on account of its miscellaneous character, the experimental matter is included in the discussion of each particular reaction.

Di-iodo-ethyl Sulfide, -sulfoxide, and -sulfone.—The replacing of the chlorine atoms is easily carried out in each case by refluxing for 2 hours with an alcoholic solution of sodium iodide. The iodo compounds are obtained in good yields. They are much less soluble in water and alcohol than the corresponding chloro compounds. It is reported that Grignard used the di-iodo-ethyl sulfide as the basis of a test for mustard gas. He passed air supposed to contain the latter through a solution of potassium iodide in water and a resultant yellowish precipitate showed a dangerous concentration of mustard gas.

The reactions involved in the preparation of the iodo derivatives are evidently



After the refluxing was over the alcohol solution and the separated crystals were poured into cold water. The di-iodo-ethyl sulfide separated in brown solid lumps, becoming yellowish white on shaking with sodium sulfite solution. Recrystallized twice out of alcohol the melting point remained at 55–60°. This substance darkened slowly at room temperature and at elevated temperatures rapidly became black. It is insoluble in water, very slowly hydrolyzed by alkali, only slightly soluble in cold and moderately in hot alcohol. The determination of iodine by decomposition with sodium ethylate and weighing as silver iodide gave 75.09% and 74.83%, calc. 74.27%.

The di-iodo-ethyl sulfoxide was obtained first as brown crystal product but after recrystallization out of alcohol became almost white and melted constant at 104.5° (corr.). It is easily soluble in hot alcohol but only moderately so in hot water. It crystallizes from water in small needles. Analysis gave 70.45% and 70.81% iodine, calc. 70.95%.

Di-iodo-ethyl sulfone was obtained as a white crystal product, recrystallizing out of alcohol in beautiful fine needles melting at 203° after softening at 198°. It was practically insoluble in water and cold alcohol and only moderately soluble in hot alcohol. It was the most stable of the iodo-derivatives. Analysis gave 68.46 and 68.14% iodine, calc., 67.91%.

Bis-β-thio-ethyl Acetate,¹ $\text{S}(\text{CH}_2\text{CH}_2\text{OOCCH}_3)_2$.—This compound,

¹ It is impossible that the oil which Clarke (*J. Chem. Soc.*, 1912, 1585 (1912)), observed could have been this diacetate, for it would have been completely hydrolyzed in his procedure.

which is the diacetate of the "mustard residue," $S(CH_2CH_2)_2$, was obtained only with considerable difficulty. Several attempts to prepare it by the reaction of sodium acetate on dichloro-ethyl sulfide in alcohol solution failed, owing to hydrolysis and alcoholysis. The sodium chloride separated and the odor of ethyl acetate was distinct but none of the desired product was obtained. It was found that the desired reaction took place smoothly and in good yield if carried out in glacial acetic acid solution:



Thus 15 g. of anhydrous sodium acetate was heated with 13 g. of dichloro-ethyl sulfide in 50 g. of glacial acetic acid on a steam bath for 6 hours. The sodium chloride was filtered off and the oil distilled *in vacuo*. After taking off the acetic acid up to 100° at 30 mm. the rest came over practically constant at $155-6^\circ$ at 20 mm. d_{20}^{20} , 1.132; n_D^{22} , 1.4720. This did not freeze at -20° . It is rapidly hydrolyzed by water. Advantage was taken of this in checking the composition.

1.4492 g. of diacetate was heated on a steam bath with 150 cc. of 0.1124 *N* potassium hydroxide solution for 2 hours. The excess of alkali was found by titration to be 25.0 cc.; whence the alkali used was 0.01405 mole. Theory requires 0.01407 mole according to the equation



Miscellaneous Reactions.

Finally there have been a number of other reactions more or less superficially investigated but, on account of lack of time, without isolating the derivatives which are assumed.

Satisfactory evidence has been obtained to show that dichloro-ethyl sulfide forms sulfonium compounds. Thus a solution of 0.2 g. of the sulfide with 0.7 g. of methyl iodide in 20 cc. of 70% alcohol had originally at 50° in a certain cell a resistance of 2100 ohms but after 4 hours at this temperature the resistance had dropped to 8 ohms. This great rise in conductivity can only be explained by the formation of a strong electrolyte, such as a sulfonium iodide, in the solution. Neither the rapidity of the rise in conductance nor the actual amount of the rise could be explained by hydrolysis. This was apparent from parallel experiments in which the dichloro-ethyl sulfide was hydrolyzed not by water, as would have to be the case above, but by alcoholic sodium hydroxide.

The Friedel-Craft's reaction between dichloro-ethyl sulfide and benzene or toluene in the presence of aluminum chloride has been found to proceed smoothly and to yield waxy solids. Several attempts to prepare the Grignard reagent from dichloro-ethyl sulfide failed, as did also an attempt to remove the chlorine by sodium in absolute ether as in the Wurtz synthesis.

In closing it is desired to direct attention to the manifold variations among these derivatives, their interesting possibilities and the wide opportunities for further research in this field.

Conclusions.

The reactivity of the chlorine atoms in dichloro-ethyl sulfide and its oxidation products has been demonstrated. The study of this reactivity has led to several new types of derivatives. Compounds of the type, $\text{RSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SR}$, were investigated where "R" was either aromatic or aliphatic. The remarkable stability of the sulfur-carbon chains has appeared of general nature. Of the structure, $(\text{ROCH}_2\text{CH}_2)_2\text{S}$ it was found that only those products could be obtained where "R" is an aromatic radical. Thus it seems that the stability of this structure is quite dependent on the nature of the radical "R." The tendency towards the formation of a heterocyclic 6-membered ring seems especially strong. This is brought out not only in the thiazan and sulfonazan condensations, but also in the formation of the substances diethylene disulfide, $\text{S} < (\text{CH}_2\text{CH}_2)_2 > \text{S}$ and diethylene sulfide-sulfone $\text{S} < (\text{CH}_2\text{CH}_2)_2 > \text{SO}_2$. The rapidity of hydrolysis of the diacetate, $(\text{CH}_3\text{COOCH}_2\text{CH}_2)_2\text{S}$, which may be regarded as 2 molecules of ethyl acetate linked together by the replacement of a β -hydrogen atom in each ethyl group by one sulfur atom, points out clearly the decrease in esterifying power effected by such substitution.

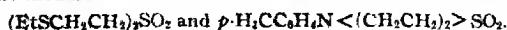
Physiological Effects.

A large number of the compounds prepared have been submitted to Dr. E. K. Marshall, Jr., and Mr. J. W. Williams, Jr., for study in the Pharmacological Laboratory of Washington University, St. Louis. We are indebted to them for the following brief summary of their findings. They will publish a more complete report in the *Journal of Pharmacology and Experimental Therapeutics*.

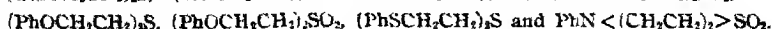
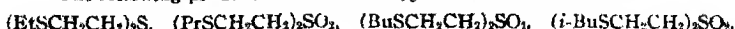
"In view of the related structure of these compounds to the highly physiologically active *dichloro-ethyl sulfide*, it is interesting to examine their physiological properties. The slight solubility of most of the compounds in water, and sometimes even in alcohol or olive oil has rendered this extremely difficult. A number of the compounds have had to be omitted entirely on account of their being so nearly insoluble in water and in olive oil.

"*Mustard gas* is a very active skin irritant, but the susceptibility of different individuals varies widely. *Dichloro-ethyl sulfoxide* produced mild erythema in one susceptible individual only, and does not appear to possess the typical skin irritant action of *mustard gas*. *Dichloro-ethyl sulfone* in aqueous alcoholic, or olive oil solution, produces an effect on the skin which appears to be similar in all respects to that produced by *mustard gas*. Typical vesicles with edema, and erythema were produced with a 5% alcoholic solution. A 1% solution in olive oil produced a positive reaction in only one out of four individuals tried. It appears, therefore, to be less active than the sulfide. The *di-iodo-ethyl sulfoxide* resembled the corresponding chlorine compound, giving a slight erythema in one individual. *Di-iodo-ethyl sulfoxide* is very

insoluble but a 0.5% solution in alcohol produced positive reactions in two out of four individuals tried. The di-acetate derivative applied as the pure oil produced mild reactions in all individuals tried. It is much less active than mustard gas. The following compounds in 1% solution in olive oil produced no reaction when applied to the skin of two individuals who were very susceptible to mustard gas, and the other compounds mentioned above:

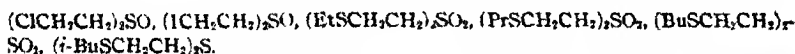


"The following produced no effect in 2% solution in olive oil:

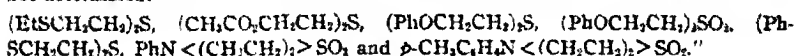


"All substances were tested in saturated aqueous solution for antiseptic or bactericidal properties against *bacillus coli* and *staphylococcus aureus*. The great majority showed absolutely no indication of any antiseptic or bactericidal power, a few showed some slight antiseptic power; and $(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$ and $(\text{ICH}_2\text{CH}_2)_2\text{SO}_2$ killed the organisms in 24 hours, but not in one hour. Further investigation revealed that the antiseptic properties of these substances were not of a high order. Incidentally these are among the most toxic of the derivatives for animals, and both irritate the skin.

"The compounds were dissolved in olive oil and the toxicity tested by subcutaneous injection into white mice. The *di-iodo-ethyl sulfone* and *dichloro-ethyl sulfone* are the most toxic of the compounds investigated, the former being considerably more toxic than the latter. The other compounds can be arranged in the order of their toxicity as follows:



The following compounds are all less toxic than the above, but the fatal dose was not determined:

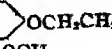




Summary.

The following new compounds have been prepared:—

Name.	Formula.	M. p.
Bis(β -chloro-ethyl) sulfoxide.....	$(\text{ClCH}_2\text{CH}_2)_2\text{SO}$	109.5°
Bis(β -chloro-ethyl) sulfone....	$(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$	56.0°
Bis(β -iodo-ethyl) sulfide.....	$(\text{ICH}_2\text{CH}_2)_2\text{S}$	55–60°
Bis(β -iodo-ethyl) sulfoxide.	$(\text{ICH}_2\text{CH}_2)_2\text{SO}$	104.5°
Bis(β -iodo-ethyl) sulfone....	$(\text{ICH}_2\text{CH}_2)_2\text{SO}_2$	203° 0
Bis(β -phenyl-mercapto-ethyl) sulfide....	$(\text{PhSCH}_2\text{CH}_2)_2\text{S}$	57.5°
Bis(β -phenyl-mercapto-ethyl) sulfoxide..	$(\text{PhSCH}_2\text{CH}_2)_2\text{SO}$	121.0°
Bis(β -phenyl-mercapto-ethyl) sulfone..	$(\text{PhSCH}_2\text{CH}_2)_2\text{SO}_2$	104.5°
Bis(β -phenyl-sulfinyl-ethyl) sulfoxide ..	$(\text{PhSOCH}_2\text{CH}_2)_2\text{SO}$	161° 0
Bis(β -phenyl-sulfinyl-ethyl) sulfone....	$(\text{PhSOCH}_2\text{CH}_2)_2\text{SO}_2$	164° 0
Bis(β -phenyl-sulfonyl-ethyl) sulfone....	$(\text{PhSO}_2\text{CH}_2\text{CH}_2)_2\text{SO}_2$	235° 0
Bis(β -phenoxy-ethyl) sulfide.....	$(\text{PhOCH}_2\text{CH}_2)_2\text{S}$	54.2°
Bis(β -phenoxy-ethyl) sulfone....	$(\text{PhOCH}_2\text{CH}_2)_2\text{SO}_2$	108.0°
Bis(β - <i>p</i> -cresoxy-ethyl) sulfide.....	$(p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2)_2\text{S}$	78.0°
Bis(β - <i>p</i> -cresoxy-ethyl) sulfone.....	$(p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2)_2\text{SO}_2$	120.0°
Bis(β - <i>o</i> -cresoxy-ethyl) sulfide.....	$(\text{CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2)_2\text{S}$	46.5°
Bis(β , α -naphthoxy-ethyl) sulfide.....	$(\alpha\text{-C}_{10}\text{H}_7\text{OCH}_2\text{CH}_2)_2\text{S}$	94.5°

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Name	Formula.	M. p.
Bis(β , β -naphthoxy-ethyl) sulfide	(β -C ₁₀ H ₇ OCH ₂ CH ₂) ₂ S	139.0°
Bis(β , β -naphthoxy-ethyl) sulfone	(β -C ₁₀ H ₇ OCH ₂ CH ₂) ₂ SO ₂	151.0°
Bis(β -vanilloxy-ethyl) sulfide	(OHC  OCH ₂ CH ₂) ₂ S	131.5°
Bis(β -eugenoxo-ethyl) sulfide.	(CH ₂ = CHCH ₂  OCH ₂ CH ₂) ₂ S	113.5°
Bis(β -tribromo-phenoxy-ethyl) sulfide	(Br  OCH ₂ CH ₂) ₂ S	118.5°
Bis(β -butyl-mercapto-ethyl) sulfide	(BuSCH ₂ CH ₂) ₂ S	b p 222-3° 17.5°
Bis(β -butyl-mercapto-ethyl) sulfoxide	(BuSCH ₂ CH ₂) ₂ SO	25.0°
Bis(β -butyl-mercapto-ethyl) sulfone	(BuSCH ₂ CH ₂) ₂ SO ₂	73.7°
Bis(β -butyl-sulfinyl-ethyl) sulfoxide	(BuSOCH ₂ CH ₂) ₂ SO	196.0°
Bis(β -butyl-sulfinyl-ethyl) sulfone	(BuSOCH ₂ CH ₂) ₂ SO ₂	171.0°
Bis(β -butyl-sulfonyl-ethyl) sulfone	(BuSO ₂ CH ₂ CH ₂) ₂ SO ₂	266.5°
Bis(β -ethyl-mercapto-ethyl) sulfide	(EtSCH ₂ CH ₂) ₂ S	b p 173-5° 17.0°
Bis(β -ethyl-mercapto-ethyl) sulfoxide	(EtSCH ₂ CH ₂) ₂ SO	64.0°
Bis(β -ethyl-mercapto-ethyl) sulfone	(EtSCH ₂ CH ₂) ₂ SO ₂	223.0°
Bis(β -methyl-mercapto-ethyl) sulfone	(MeSCH ₂ CH ₂) ₂ SO ₂	77.0°
Bis(β -propyl-mercapto-ethyl) sulfide	(PrSCH ₂ CH ₂) ₂ S	b p 193-5° 27.5°
Bis(β -propyl-mercapto-ethyl) sulfoxide	(PrSCH ₂ CH ₂) ₂ SO	75.5°
Bis(β -propyl-mercapto-ethyl) sulfone	(PrSCH ₂ CH ₂) ₂ SO ₂	254.0°
Bis(β -isobutyl-mercapto-ethyl) sulfone	(i-BuSCH ₂ CH ₂) ₂ SO ₂	94.2°
Bis(β -sec-butyl-mercapto-ethyl) sulfone	((sec)BuSCH ₂ CH ₂) ₂ SO ₂	15.0°
Bis(β -amyl mercapto-ethyl) sulfide	(AmSCH ₂ CH ₂) ₂ S	20.0°
Bis(β -amyl mercapto-ethyl) sulfone	(AmSCH ₂ CH ₂) ₂ SO ₂	91.0°
4-Phenyl-1,4-thiazan	Ph N < (CH ₂ CH ₂) ₂ > S	108-111°
4-Phenyl-1,4-sulfanazan	Ph N < (CH ₂ CH ₂) ₂ < SO	123.5°
4-p-Cresyl-1,4-sulfonazan .	p CH ₃ C ₆ H ₄ N < (CH ₂ CH ₂) ₂ > SO ₂	136.5°
4-o-Cresyl-1,4-sulfonazan	o CH ₃ C ₆ H ₄ N < (CH ₂ CH ₂) ₂ > SO ₂	135.0°
Bis(β -thio-ethyl acetate)	(CH ₃ COOCH ₂ CH ₂) ₂ S	b p 155-6° (20 mm.)

BALTIMORE, MD

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, HARVARD UNIVERSITY.]

ON THE NONEXISTENCE OF VALENCE AND ELECTRONIC ISOMERISM IN HYDROXYLAMMONIUM DERIVATIVES.

By ARTHUR MICHAEL

Received March 9, 1920

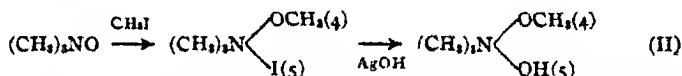
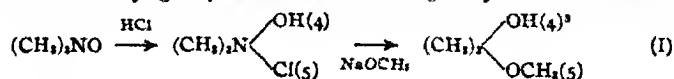
In 1894, Dunstan and Goulding¹ showed that trimethyl-hydroxylammonium iodide is the sole substitution product formed in the action of methyl iodide on an excess of hydroxylamine; later,² that the base set free from that salt represents a hydrated trimethylamine oxide. Further, that methyl iodide unites at ordinary temperature with the product to give the iodide of an ammonium base, to which they assigned the structure

¹ *Proc. Chem. Soc.*, 10, 138 (1894); *Chem. News*, 69, 308 (1894).

² *J. Chem. Soc.*, 69, 839 (1896); 75, 792, 1005 (1899).

$(\text{CH}_3)_3\text{N}(\text{OCH}_3)\text{I}$, and which is decomposed by caustic potash into the amine oxide and methyl alcohol. A later examination of these reactions and products by Meisenheimer¹ has led to results and conclusions of great theoretical interest. This chemist, who prepared the amine oxide in a free state, found that the hydroxide obtained from the addition product with methyl iodide is capable of existing only in dil. aqueous solution, and decomposes on evaporation of the solvent into trimethylamine and formaldehyde, not into the amine oxide and methyl alcohol, as Dunstan and Goulding believed. On the other hand, by treating the amine oxide chlorohydrate with sodium methylate dissolved in absolute methyl alcohol, a solution was obtained which left the amine oxide as a residue on evaporation.

Meisenheimer² had previously assumed the particular valence in ammonium derivatives uniting the nitrogen with the acid radical to be different from the 4 other valences. Representing this valence by (5), it is evident that the structures of these 2 bases are identical, except that the hydroxyl and methoxyl groups are linked to nitrogen by different valences:



The existence of this remarkable kind of valence isomerism⁴ was further confirmed by preparing 3 pairs of similarly constituted, bisubstituted derivatives that show the same striking contrast in the products of decomposition. For instance, the compound from the amine oxide and methyl iodide yields, by double decomposition with sodium ethylate or propylate, products that break up on evaporation of the alcoholic solution into trimethylamine, formaldehyde and ethyl or propyl alcohol. On the other hand, the isomeric derivatives, obtained from the addition products of ethyl and propyl iodides and sodium methylate, decompose

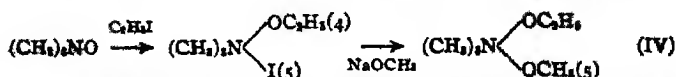
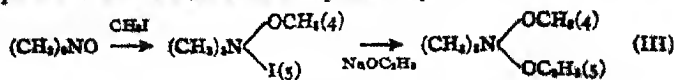
¹ *Ann.*, 397, 273 (1913).

² *Ibid.*, 385, 117 (1911).

³ There is no decisive evidence that the solution before evaporation contained this product, as the reaction may proceed through the formation of $(\text{CH}_3)_3\text{N}(\text{ONa})\text{Cl}$, which would decompose into the amine oxide and salt.

⁴ Meisenheimer (*Ann.*, 397, 273 (1913)), believes that the non-equivalence or inequality of the 5 nitrogen valences is the cause of the assumed isomerism, and it seems, therefore, appropriate to designate its valence isomerism; although Werner has used that expression in a somewhat different sense. It is hardly conceivable that the bond energy holding the chlorine and hydrogen in the ammonium chloride molecule is equal in value, and, from that point of view, an inequality certainly exists between the energy relations in these atoms. It cannot cause isomerism, however, as a readjustment in the energy relations must take place with a chemical change in the molecule.

into ethyl, resp., propyl aldehyde, methyl alcohol and trimethylamine. The preparations and isomerism are expressed by:

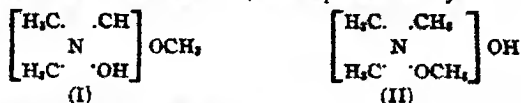


Meisenheimer calls attention to the fact, that it is always the alkyl radical joined by valence (4) which is split off as an aldehyde, and believes the "reaction proves that the two alkylxyl groups are not joined to the nitrogen atom in the same manner."¹ Willstätter² had suggested "oxonium" structures for the salts of the amine oxide, and also for the hydrated base, but Hantzsch and Graf³ showed experimentally that the properties of the compounds are not compatible with such an interpretation. Later, Werner⁴ expressed a similar view in terms of his ammonium hypothesis, but Meisenheimer in the first paper,⁵ and later,⁶ in a discussion of the subject with Fromm,⁷ showed that the suggestion is not tenable.

Meisenheimer's explanation is based on a modified interpretation of Werner's ammonium hypothesis, and he assigns the following structures to III and IV:



but with the reservation that they only represent the structures correctly, if, in opposition to Werner's views, "all five radicals are joined to nitrogen by main valences, four in the inner and one in the outer zone."⁸ According to this interpretation the isomeric trimethyl-methoxylammonium hydrates, designated above as I and II, are represented by:



The subject has also been considered by L. W. Jones⁹ from the viewpoint of the "electronic" hypothesis. This chemist assumes that the methoxyl

¹ *Loc. cit.*, 277.

² *Ber.*, 33, 1638 (1900).

³ *Ibid.*, 38, 2154 (1913).

⁴ "Neuere Anschauungen," pp. 210, 204 (1909).

⁵ *Loc. cit.*, 278.

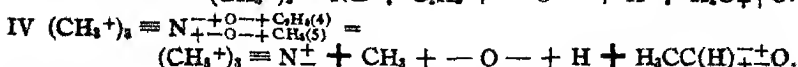
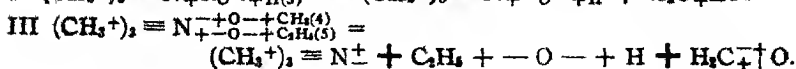
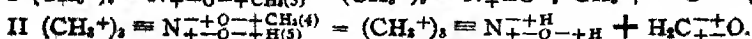
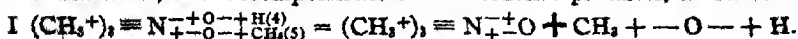
⁶ *Ann.*, 399, 371 (1913).

⁷ *Ibid.*, 366 and 377.

⁸ *Ann.*, 397, 283 (1913).

⁹ *This Journal*, 36, 1284-88 (1914).

group is positive in II and III and negative in I and IV, and represents the isomerism, and decompositions of the isomeric products, as follows:



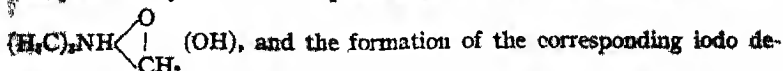
It is evident that the acceptance of either of these interpretations involves far-reaching modifications in the present conception of valence and its relation to chemical properties. Even if it were granted that the values of the valences joining the hydroxyl and methoxyl groups to the nitrogen in I and II differ quantitatively, or in the "electronic" relations, there is no precedent in chemistry for the assumption that a methoxyl group on hydrolysis should yield formic aldehyde; on the contrary, all established facts point unmistakably to that of methyl alcohol. If it is admitted that the valence of an atom may exist in several modifications, and that these may cause such radical differences in chemical properties, then a permanent correlation between the valence theory and chemical behavior no longer exists, and the theory will lose much of its precision and usefulness in coordinating properties with structure. These remarks apply also to the explanations given for the breaking up of III and IV in differ-

ent directions. The properties of substances of the type $\text{R} \begin{array}{l} \text{OCH}_3 \\ \text{OC}_2\text{H}_5 \end{array}$

are well established, and, without exception, they show considerable stability towards heat energy. To suppose that the hydroxylammonium derivatives have such structures, and, notwithstanding, are so unstable that they break up on evaporation of the absolute alcoholic solution *in vacuo* is scarcely conceivable chemically. And, quite as much opposed to chemical precedents, is the formation of aldehydes and different products of decomposition from substances with such structures, irrespectively whether they are interpreted according to the Werner hypothesis, or, whether with Jones, positive and negative signs are arbitrarily connected with certain of the atoms.

There is, however, no necessity to modify our conceptions on the relations between the valence phenomenon and the structures and chemical properties of substances. Derivative I, if it is formed in the action of sodium methylate on the chlorohydrate of the amine oxide, must have the formula $(\text{H}_3\text{C})_3\text{N}(\text{OH})\text{OCH}_3$, and such a derivative should decompose easily into the amine oxide and methyl alcohol. The isomeric product II, which is prepared from the addition product of the amine oxide and

methyl iodide by double decomposition with silver oxide, has the structure



rivative becomes evident when the properties of organic nitroso compounds are taken into consideration.

Dunstan and Goulding's assumption that methyl iodide adds to the amine oxide to form a methoxylammonium salt certainly appears to be a consistent theoretical conclusion, and, that the addition does not proceed in this manner, is due to the following reasons. Owing to the presence of the negative hydroxyl group, hydroxylammonium hydrate has much less strongly developed basic properties than ammonium hydrate,¹ which manifests itself in the marked tendency to form stable halhydric salts with the acid component in a smaller molecular proportion than in the corresponding ammonium salts,² indeed, as by-products in the preparation of trimethyl amine oxide, di- and trihydroxylamine iodohydrates are formed, but none of the normal salt.³ The intramolecular neutralization of the atomic forces in trimethyl-methoxylammonium iodide is, therefore, less complete than in the tetramethyl ammonium compound, and the tendency to form a derivative of that type should be less pronounced. The course of the addition of alkyl iodides to the amine oxide is mainly directed, however, by the energy and affinity relations of the atoms in the nitroso group, that are so characteristically shown in the spontaneous isomerization of the primary and secondary nitrosoalkanes to oximes. Trimethylamine oxide also contains a nitroso group, but, like the tertiary nitrosoalkanes, it represents a stable product under ordinary conditions, because the free energy in the atoms of the group has been converted to a very considerable extent into bound energy and heat, through the direct and spatial intramolecular action of the numerous hydrogen and carbon atoms.

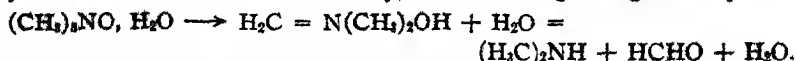
According to the le Chatelier-van't Hoff equilibrium law the effect of heat on the structure of trimethylamine oxide should be to strive to change it into one with a greater energy content. It may be expected, therefore, that at a certain temperature the amine oxide will have absorbed sufficient energy to isomerize to $(\text{H}_3\text{C}) = \text{N}(\text{CH}_3)_2\text{OH}$; a change that is favored by the increase in the affinity relation of hydrogen for oxygen over that for carbon with the rise of temperature. The isomerized substance represents a condensation product of an aldehyde and dimethylammonium hydrate, and, as such derivatives are very easily hydrolyzed, and, as the hydrated amine oxide on heating under ordinary pressure

¹ Mac Kay, *Centr.*, 1908, I, 1918.

² Lowsen, *Ann.*, 160, 242 (1871).

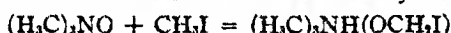
³ Dunstan and Goulding, *loc. cit.*

parts with its water with difficulty,¹ the following changes take place:²



On heating the amine oxide sulfate with dil. sulfuric acid, formaldehyde and dimethylammonium sulfate are formed, and at a much lower temperature (110°).³ The decomposition is greatly facilitated under these conditions, for, in starting from the sulfate, a product much richer in free energy is not only used, but the quality is such, that it will be largely converted into bound energy and heat by the strong base formed in the reaction. Then, the affinity of the hydroxyl group for nitrogen, and that of the methyl hydrogen atom for the carbon, is decreased by such negative influence,⁴ and the additive capacity of water to unsaturated compounds is enormously accelerated by the intramolecular, dynamic conditions prevailing in the dilute, aqueous solution of the acid.⁵

The isomerization of nitrosomethane to formaldoxime represents an intramolecular reduction of the oxygen and oxidation of the carbon; the hydrogen passing over to the oxygen not only on account of the quality and quantity of the free energy in it, but because in so doing an intramolecularly well-neutralized, amphoteric substance is formed.⁶ The other course of isomerization is evidently barred, for a substance with the formula $\text{H}_2\text{C} = \text{NH}(=\text{O})$ would be vastly richer in free energy; indeed, if it could be prepared in another way, it should, on account of the much greater affinity of hydrogen for oxygen than for nitrogen and the energetic relations in these atoms, spontaneously convert itself into the oxime. The primary reaction between the amine oxide and methyl iodide



represents an intermolecular reduction of the nitrogen and an oxidation of the carbon in the iodide. A hydrogen of the iodide passes over to the nitrogen, for the contrary course of addition would lead to the formation of iodomethyl-trimethylammonium hydrate, $(\text{H}_2\text{Cl})(\text{H}_3\text{C})_3\text{NOH}$, which would be a strongly basic substance, and, as it would have a far greater content in free energy, its production would not represent the possible maximum entropy of the reaction.⁷ The formula $(\text{H}_3\text{C})_3\text{NH}$

¹ Dunstan and Goulding, *J. Chem. Soc.*, 75, 796 (1899).

² *Loc. cit.* Dunstan and Goulding state, "near 180° the base suffers decomposition, formaldehyde and trimethylamine being among the products," but give no analytical details. There can be no doubt that dimethylamine must also be formed, as otherwise the appearance of formaldehyde would be quite inexplicable.

³ *Loc. cit.*

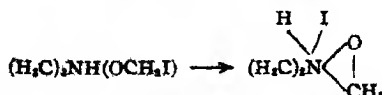
⁴ *THIS JOURNAL*, 32, 996 (1910).

⁵ Michael and Brunel, *Am. Chem. J.*, 41, 118 (1909); 48, 266 (1912).

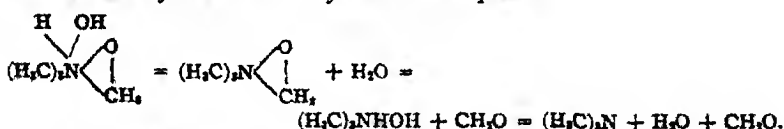
⁶ Michael, *THIS JOURNAL*, 32, 1000 (1910).

⁷ Meisenheimer (*loc. cit.*, 289) found that ethyl and propyl iodides scarcely react on the hydrated, but readily on the anhydrous amine oxide. This difference in be-

(OCH₂I) is evidently in accord with the formation of trimethylamine and formaldehyde by hydrolysis, but not with that of a platinumchloride and aurichloride from the corresponding chloro derivative, nor with the great chemical mobility of the halogen atom. In fact, all the addition products of the amine oxides and alkyl iodides act like salts of not very strong bases, as they are hydrolyzed by water to the extent of forming strongly acidic solutions.¹ It must be assumed, therefore, that the CH₂I group in the above compound reacts intramolecularly and additively on the basic nitrogen atom



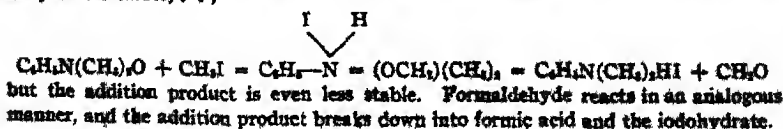
to form the hydriodic acid salt of a condensation derivative of the unstable trimethylammonium hydrate and formaldehyde. This structure complies in every respect with the properties of the substance. The iodo compound, which may be called form-trimethyl-ammoniumhydroxide hydriodide, owes its comparative stability to the intramolecular conversion of positive energy, centered at the nitrogen atom, by the negative of the halogen,² and a corresponding decrease in that property follows the replacement of the halogen by the much less negative hydroxyl group. Indeed, the hydroxide may exist only for a short time even in aqueous solution, and on evaporation of the solvent, a quantitative decomposition into formaldehyde and trimethylamine takes place:³



The properties and decompositions of the isomeric compounds, obtained havior is undoubtedly due to the loss of free energy in the nitroso group accompanying hydration; the oxide is extremely hygroscopic, and the process undoubtedly proceeds exothermically, *i. e.*, with conversion of some of its free chemical energy into heat.

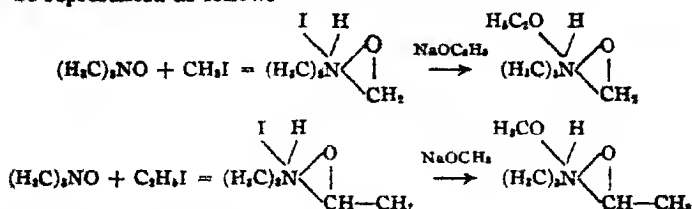
¹ Hantzsch and Graf (*Ber.*, 38, 2156 (1905)) believe that a slight hydrolysis only takes place with solution, but Meisenheimer (*loc. cit.*, 284) states that the solutions are strongly acidic.

² Bamberger and Techimer (*Ber.*, 32, 1886 (1899)) found that the less basic dimethylaniline oxide with methyl iodide gives formaldehyde and dimethylaniline iodohydrate on standing. This reaction proceeds in a similar manner to that with the fatty amine oxides, *i. e.*,



³ Meisenheimer, *loc. cit.*, 284.

on treating the addition products of the amine oxide and alkyl iodides with different alkylates, may now be explained. For instance, the reactions between the amine oxide and methyl and ethyl iodides, and those of the addition products with sodium ethylate, respectively, methylate, may be represented as follows



It is evident, that substances of these structures must be quite unstable towards heat and water; indeed, Meisenheimer¹ found that they exist only in absolute alcoholic solutions, breaking up on concentration into trimethylamine and an alcohol and aldehyde.² Further, the aldehyde must correspond to the alkyl iodide, since that product is oxidized in the addition to the amine oxide, and the carbinol to the sodium alkylate, which relations agree with Meisenheimer's results.

Remsen and Norris³ found that trimethylamine and chlorine unite to form a very unstable addition product, that decomposes easily in moist air; with bromine a somewhat more stable product, $(\text{H}_3\text{C})_3\text{NBr}_2$, was isolated, but it decomposes instantly with water, liberating an atom of the halogen as hydrobromic acid. The same product is formed in the action of bromine on trimethylammonium bromide, and this formation, together with the behavior towards water, led Norris⁴ to change the formula into $(\text{H}_3\text{C})_3\text{NBr}_2$, HBr . This conclusion implied the formation of hydrobromic acid, and it could be shown⁵ that, on adding bromine in ether to trimethylamine in the same solvent, a precipitate of the bromohydrate is deposited, as long as the base is in excess.

¹ *Loc. cit.*, 277

² The facility of decomposition into carbinols and $(\text{H}_3\text{C})_2\text{N} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CHR} \end{array}$ is self-evident;

the latter compound is a derivative of the unstable trimethylammonium hydroxide, and its existence as a derivative in solution is due to substitution of the 2 hydrogens by an alkylidene group. Cyclic derivatives of this nature are easily decomposed, even when the nitrogen is trivalent, and a ring derivative with a pentavalent nitrogen could not show more than a slight stability. Other substances containing halogen are known, in which the nitrogen has a higher valence than 5, e. g., $(\text{H}_3\text{C})_4\text{NI}_2$ and $(\text{H}_3\text{C})_4\text{NI}_2$ (Weltzien, *Ann.*, 91, 33 (1854))

³ *Am. Chem. J.*, 18, 91 (1896)

⁴ *Ibid.*, 20, 51 (1898)

⁵ *Loc. cit.*

Hantzsch and Graf¹ re-established the older formula, by showing that 2 atoms of iodine are liberated on adding potassium iodide to a solution of the substance in acetic acid. They endeavored to replace the bromine in the compound by hydroxyl, but found that metallic oxides or hydroxides give trimethylamine, with metallic bromides and hypobromites, but no amine oxide or its hydrate.² Hantzsch³ used these results for speculations on the constitution of ammonium salts, and on the mechanism of double decomposition, which have a bearing on the subject discussed in this paper. That chemist compares the behavior of the amine dibromide with that of lead bromide



and believes the amine dibromide should react in a corresponding manner. For trimethyl-hydroxylammonium bromide represents a "very stable salt,"⁴ and the amine oxide is fairly stable. Hantzsch⁴ believes the decomposition of the amine dibromide by potash into amine and hypobromous acid to be unexplainable from the commonly accepted structure of the compound; since $(\text{H}_3\text{C})_3\text{N(OH)Br}$ should be the intermediate product of the reaction, and that substance cannot decompose in the above manner. He finds, however, an "entirely satisfactory" explanation of these results in Werner's ammonium hypothesis, and, accordingly, expresses the addition products with hydrobromic acid and bromine by $[\text{N}(\text{CH}_3)_3\text{H}]\text{Br}$ and $[\text{N}(\text{CH}_3)_3\text{Br}]\text{Br}$. The latter product should yield bromo-trimethylammonium hydrate, $[\text{N}(\text{CH}_3)_3\text{Br}]\text{OH}$, on hydrolysis, which should break up into trimethylamine and hypobromous acid.⁵

The behavior of triethylamine towards chlorine water has recently been studied by Meisenheimer,⁶ who shows that it is converted into a mixture of the chlorohydrates of di- and tri-ethylamine and acetaldehyde. This interesting result is explained⁷ by the decomposition of the first-formed product, $(\text{H}_5\text{C}_2)_3\text{NCl}_2$, into hydrogen chloride $(\text{H}_5\text{C}_2)_2(\text{CH}_2\text{CH}=\text{O})\text{NCl}$, and the hydrolysis of the latter substance into diethylamine chlorohydrate and aldehyde; the acid set free unites with unchanged tertiary base, and protects it from the action of the halogen. It is now possible to explain the apparently anomalous results obtained by Remsen and Norris in the behavior of bromine towards trimethylamine in excess, and that of the amine dibromide towards water. In the first reaction, some of the

¹ Ber., 38, 2157 (1905).

² Ibid., 2161.

³ Ibid., 2162.

⁴ Loc. cit.

⁵ Ibid., 2163.

⁶ Ber., 46, 1160 (1913).

⁷ Ibid., 1150.

amine forms the dibromide, which reacts with unchanged base to form a not isolated product,¹ undoubtedly $(\text{H}_3\text{C})_2(\text{H}_2\text{C}=\text{N})\text{NBr}$, and the salt of the tertiary base. The amine dibromide with cold water undergoes the same decomposition, liberating $1/2$ of the halogen as hydrobromic acid.

The behavior of the trimethylamine dihalides towards water is a characteristic organic reaction.² The ease of the elimination process is due to the loosening of the affinity between carbon and hydrogen by the negative NHal_2 group,³ and the slight affinity between nitrogen and halogen; the following phase is facilitated by the quality and quantity of the free energy at the unsaturated carbon and nitrogen of the intermediate product, $(\text{H}_3\text{C})_2(\text{H}_2\text{C}=\text{N})\text{NHal}$, for water. With the formation of dimethylammonium halhydrate, the free energy in the NHal group is very largely converted into bound energy and heat, and the possible maximum increase of entropy in the system is realized.

The course of decomposition of the amine dibromide by water is determined by the strong affinity of water for hydrobromic acid, and the comparatively weak affinity for bromine. With the addition of alkali to the mixture a substance with a great capacity to directly neutralize the free chemical energy in the halogen atoms is introduced into the system, and, as the expenditure of energy necessary to separate them from the nitrogen atom is inconsiderable, the amine dihalide behaves chemically as if it were practically a mixture of amine and halogen. A second determining factor for this course of the reaction is the slight affinity of oxygen for nitrogen, which is so manifest in the negative values of the heats of formation of the oxides of nitrogen, and remains comparatively small, irrespective of the elements or groups to which the nitrogen atom may be joined.⁴ For these reasons, when halogen in an organic substance is in direct union with nitrogen, it cannot be replaced by oxygen or hydroxyl. The reactions proceed either, (1) with the elimination of halhydric acid, (2) the direct removal of the halogen, or (3) its replacement by hydrogen, according to the chemical nature and structure of the substance, and the chemical character of the reagents.

When the behavior of trimethylamine dibromide and lead dibromide are viewed, not from a rigid application of the valence hypothesis, but from the affinity and energy conditions of nitrogen and lead, it is evident at once that similar reactions could not be expected. Nitrogen has only a small affinity for oxygen and much less for halogen, decreasing from iodine to bromine and then to chlorine; even when it is joined to 3

¹ Norris, *loc. cit.*, 63.

² The dialkylchloroamines are decomposed by alkali in a similar manner (Berg, *Ann. chim. phys.*, [7] 3, 344 (1894)).

³ *THIS JOURNAL*, 32, 996 (1910).

⁴ Berthelot and André, *Compt. rend.*, 110, 836 (1890).

alkyl groups, the affinity of nitrogen for halogen is slight, as is evident from the properties of the compounds. And, as these addition products are formed with a small conversion only of the free energy in the halogen atom into bound energy with the nitrogen atom, the energetic hindrance to a dissociation into the component parts is inconsiderable. On the other hand, the affinity of lead increases from oxygen to halogen, *i. e.*, in exactly the reverse relationship. And, a very considerable expenditure of energy is required to separate it from halogen, as the free energy of the halogen and of the metal has been largely converted in their union into bound energy and heat. The reaction between lead bromide and caustic alkali proceeds by double decomposition, because lead has a decided affinity for oxygen, as is shown in the considerable heat of formation of lead oxide and hydroxide, and the entropy increase with the formation of the latter compound and alkali bromide, must be far greater than it would be with that of metallic lead, alkali bromide and hypobromite.

Willstätter and Iglaue¹ found that hypochlorous acid reacts upon the tertiary base tropidine to form the N-chloro derivative of the secondary base norotropidine, and explained the result by assuming a decomposition of the primary product, $R(CH_3)N(OH)Cl$, into $RNCl$ and CH_3OH . Hantzsch and Graf² showed that trimethylamine and hypochlorous acid form at first the corresponding hypochlorite, and then dimethylchloroamine. Under the supposition that methyl alcohol is the second product of the reaction, Hantzsch³ explains the result by assuming that the acid may ionize to a slight extent also into $Cl^- + OH^-$, and that it should, therefore, form some $[(H_3C)_3NCl]OH$, which may break up into base and acid, or into the chloroamine and the carbinol. Even if the unproven and very doubtful ionization of hypochlorous acid into $Cl^- + OH^-$ be accepted, the addition of these ions to the amine⁴ must proceed with the possible maximum increase of entropy, that is with the formation of the salt derivative, $[(H_3C)_3N(OH)]Cl$, and not with that of the basic substance $[(H_3C)_3NCl]OH$. But the first structure represents the product obtained from the amine oxide and hydrochloric acid, and that salt does not decompose in the manner assumed by Hantzsch.

¹ *Ber.*, 33, 1636 (1900).

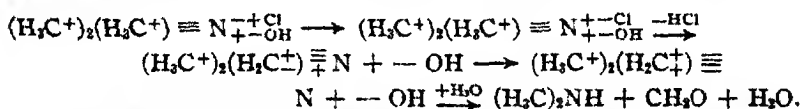
² *Ibid.*, 38, 2156 (1905).

³ *Ibid.*, 2163.

⁴ Hypochlorous acid is always used in very dilute solution and must add as an electrolyte, to form primarily a hypochlorite, which may rearrange to a more stable chlorohydrol (Michael, *J. prakt. Chem.*, [2] 60, 452, 463 (1899); Michael and Leighton, *Ber.*, 39, 2157 (1906)). This assumption is essential to explain the course of such additions to unsaturated hydrocarbons. It is, therefore, unnecessary to suppose the presence of traces of $Cl^- + OH^-$, as the unstable amine hypochlorite may directly rearrange to the more stable chlorohydrol, but in that case, too, trimethylhydroxylammonium chloride should be formed.

Meisenheimer¹ showed later that hypochlorous acid does not react upon trimethylammonium chloride, and that it gives dimethylchloroamine in very small amounts with the free base. But better yields of that product are obtained by using the chloride and sodium or calcium hypochlorites, although these salts must be taken in a large excess. When 2 mol. equivalents only of the salts are used practically no chloroamine is formed, and the products are unchanged tertiary amine, with some dimethylamine and formaldehyde, which, and not methyl alcohol as was previously supposed, is the second product formed under all conditions. Meisenheimer² accounts for these results by the presence of free chlorine in the reagents, which unites with the base to form the dichloride, and which on decomposition yields the products mentioned above.³

L. W. Jones⁴ objects to this experimental solution of the problem on the ground that the dichloride would not persist to any extent in an alkaline medium of the character of the hypochlorites used, but should give trimethyl-chloroammonium hydroxide.⁵ The decomposition of that product into dimethylamine and formaldehyde is explained "electronically" as follows:⁶



This explanation is untenable for several reasons. In order to lose hydrochloric acid the "electronic" signs between the nitrogen and chlorine of the primary product have to be inverted, but the "electromer" thus formed, which is the product assumed to undergo the decomposition, is no longer a derivative of chloroammonium hydroxide, but represents an unstable "electromeric" derivative of hydroxylammonium chloride, and should pass over into $(\text{H}_3\text{C}^+)_2 \equiv \text{N}^+ \begin{smallmatrix} \text{Cl} \\ \vdots \\ \text{OH} \end{smallmatrix}$. That formula, however, represents the addition product of trimethylamine oxide and hydrochloric acid, which yields the amine oxide upon treatment with alkali. Further, how is it possible for Jones to assume the formation of the chloroammonium hydroxide, as the primary product of the action of hypochlorous acid upon trimethylamine, after Meisenheimer⁷ has shown that the base may be even heated with a large excess of the acid, and yields dimethylchloroamine only in

¹ *Ber.*, 46, 1148 (1913).

² *Loc. cit.*, 1150.

³ See page 1240.

⁴ *THIS JOURNAL*, 36, 1275 (1914).

⁵ The dichloride does not "persist" (see page 1240), and the replacement of Cl by OH never occurs in such derivatives (see page 1241).

⁶ *Loc. cit.*, 1277.

⁷ *Ibid.*, 1159.

process? Evidently, the hypochlorite first formed¹ simply dissociates on heating, as hypochlorous acid would react upon dimethylamine, if it were present, to give the corresponding chloroamine.

The theoretical objections to the Meisenheimer-Werner view,² apply with equal force to the "electronic" explanation. The hypochlorite is expressed "electronically" by $(\text{H}_3\text{C}^+)_3 \equiv \text{N}^+ \text{---} \text{O}^- \text{---} \text{H}^+ \text{---} \text{Cl}^-$, which would have to change into $(\text{H}_3\text{C}^+)_3 \equiv \text{N}^+ \text{---} \text{O}^- \text{---} \text{H}^+ \text{---} \text{Cl}^-$, before it could rearrange to $(\text{H}_3\text{C}^+)_3 \equiv \text{N}^+ \text{---} \text{OH}^- \text{---} \text{Cl}^-$. That formula represents one of the possible "electromers" of trimethylhydroxylammonium chloride, and is, indeed, the stable form of the "electronic" structure, which Jones³ assumes to be formed in the addition of hypochlorous to the tertiary base, and which, as explained above, does break up by elimination of hydrochloric acid into $(\text{H}_3\text{C})_3(\text{H}_2\text{C}=\text{N})\text{NOH}$, but into the amine oxide.⁴

The "coördination" and the "electronic" formulas are structurally closely connected: $[(\text{CH}_3)_3\text{N}(\text{OH})\text{Cl}]$ and $(\text{CH}_3)_3\text{N}^+ \text{---} \text{OH}^- \text{---} \text{Cl}^-$ representing a derivative of hydroxylammonium chlorohydrate, and $[(\text{CH}_3)_3\text{NCl}]\text{OH}$ and $(\text{CH}_3)_3\text{N}^+ \text{---} \text{OH}^- \text{---} \text{Cl}^-$ one of chloroammonium hydroxide. Jones, in his endeavor to place the plus and minus signs in the "electronic" formula so as to permit the elimination of hydrochloric acid, overlooked that such a decomposition cannot possibly take place in a derivative with a salt structure. And, to conjecture on that possibility in derivatives of chloroammonium hydroxide is superfluous, as there is absolutely no experimental evidence indicating the existence of such compounds, which besides involve theoretically extremely improbable assumptions.

Conclusion.

Isomeric trialkyl-hydroxylammonium salts and trialkyl-dialkylloxylammonium derivatives are not known, and there is, therefore, no experimental

¹ Undoubtedly due to free chlorine, which is usually present in aqueous hypochlorous acid

² Hantzsch and Graf, *Ber*, 38, 2156 (1905)

³ See page 1234.

⁴ *Loc. cit.*, 1277

⁵ According to Jones (*loc. cit.*, 1278) the "electronic" formula of trimethylamine dibromide is $(\text{CH}_3^+)_3 \equiv \text{N}^+ \text{---} \text{Br}^- \text{---} \text{Br}^-$, and the substance may be completely "hydrolyzed" by alkali to form the tertiary amine and a hypobromite and bromide, or, partially into $(\text{CH}_3^+)_3 \equiv \text{N}^+ \text{---} \text{Br}^- \text{---} \text{OH}^-$, which "would be formed by the addition of hypobromous acid to trimethylamine," and "would either be hydrolyzed further, or dissociate directly into hypobromous acid and trimethylamine. On the other hand, it might undergo intramolecular oxidation, and lose formaldehyde to give dimethylamine." A further discussion of this subject does not appear necessary, but, in view of Hantzsch's proof that the dibromide is decomposed by alkali only in one way, i. e., that it practically falls apart into amine and halogen, and Meisenheimer's correction and explanation of Willstätter's abnormalities, the statement (Jones, *loc. cit.*) that these "electronic" interpretations account for all the "aberrations" observed by Hantzsch and Willstätter certainly requires elucidation

evidence in this field to support Werner's ammonium or "coördination" hypotheses, or any modifications of them. Nor, are any facts known to substantiate "electronic" conceptions, or the existence of "electromers," in this group of compounds.¹

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SOME OBSERVATIONS ON THE COLOR CHANGES OF THE DIPHENYLAMINE REACTION.

By E. M. HARVEY.

Received February 12, 1920

The diphenylamine reaction is recognized as one of the most delicate qualitative tests for nitrate nitrogen. However, the utilization of this reaction as a microchemical test for nitrates in plant tissue presents numerous difficulties. Many substances occurring as normal constituents of the cells may diminish the intensity of the characteristic blue coloration, and in some rarer instances the coloration may be completely inhibited. But besides the interference of such substances there are grosser factors influencing the reaction, so that the results of a series of tests of the same tissue may be very inconsistent.

These latter inconsistencies directed the observations on the color changes² herein reported. Solutions containing only diphenylamine, nitric acid, sulfuric acid and water were used in the study of the factors controlling the production and intensity of the coloration. The factors studied were the concentration of sulfuric acid, the temperature, time and the order of mixing.

Of these factors, the concentration of the sulfuric acid is the most important. Fig. 1 shows the influence of this concentration throughout a close series from 20 to 96% sulfuric acid. The repetition of such series has always given essentially like results. Solutions were made up in 6 cc. shell vials. The total volume of solution was 5 cc., and through a single series the quantities of nitric acid and diphenylamine were constant, as, for example, in one of the best series each vial contained 0.4 mg. of diphenylamine and 0.06 mg. of nitric acid. The lower limit of blue color-

¹ Stieglitz, (THIS JOURNAL, 38, 2033 (1916)) referring to the hydroxylammonium derivatives and to the paper by Jones, remarks "that the only electromers whose separate existence has been convincingly shown are the hydroxylamines."

² The chemistry of the reaction and its application to the qualitative determination of nitrates have been the objects of much previous work, to which some of the important references are as follows: Kehrman and St. Micewicz, *Ber.*, 45, 2641 (1912); Wieland, *ibid.*, 46, 3296 (1914); Withers and Ray, THIS JOURNAL, 33, 708 (1911); Coron, *Ann. chim. anal.*, 16, 211 (1911); Tillmans and Splittgerber, *Z. Natur. Genussm.*, 25, 417 (1913).

tion, as shown in Fig. 1, may be lowered 7% to 10%, in terms of sulfuric acid, if the sulfuric acid removed is replaced by a corresponding percentage of glacial acetic acid or potassium sulfate. This fact may indicate that the water, as such, plays a critical role in the coloration in this region of

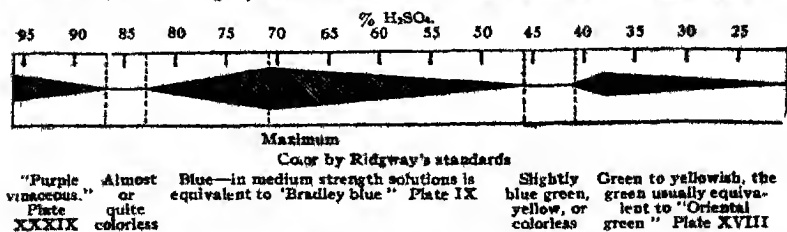


Fig. 1.—The relation of the concentration of sulfuric acid to the color changes of the diphenylamine reaction

the series. Such a supposition would appear to be in agreement with the view that the color reaction is due to an oxidation and hydration of the diphenylamine. The 3 principle colors shown in the series of Fig. 1 are probably also caused by different degrees of oxidation and hydration of the diphenylamine molecule (cf. Kehrman and St. Micewicz).

The amount of diphenylamine can be the controlling factor, but as the limits are rather wide, this is not likely to cause difficulty in any of the formulas and methods commonly recommended. Too much diphenylamine, however, interferes with the color production.

Obviously the amount of nitrate would influence the coloration, but it is not easy to take advantage of this fact for quantitative considerations, because with any favorable concentration of sulfuric acid only slight differences of color intensity are to be noted through wide variations in the amount of nitrate present.

Variable temperatures between 20° and 50° appear to have relatively slight effect, except on the time required for the development of the maximum coloration for any given mixture.

The order of mixing is sometimes of importance for the reason that the blue color is somewhat stable, and if allowed to form under local temporary conditions of concentration during mixing, will persist after the medium has reached a general concentration (as to acid, etc.), which would have otherwise precluded the production of the resulting color.

Other series of solutions were made up as described, with the exception that each vial received an addition of a chloride, usually as potassium chloride. About 2% of potassium chloride was found to intensify the color throughout the blue region of the series, causing not only an intensification of the blue color, but also producing a lengthening of the blue region toward both the high and low concentrations of the sulfuric acid. Chlorides did not appear to affect the other colors of the series.

In consideration of the above results the writer has slightly modified the usual formulas¹ for the diphenylamine reagent as used in microchemical tests for nitrates. This reagent should be applied directly to the tissue on a glass plate or microscope slide. The tissue should be cut into thin sections or, preferably, into small rather thick pieces which may then be crushed in the reagent. The modification offers some advantage in possessing a sulfuric acid and a chloride content a little above that for maximum coloration, so that, if the reagent is used liberally the moisture of the tissue will be no more than to bring the optimum conditions for best coloration.

The modified reagent is made up of 0.05 g. of diphenylamine, 7.5 cc. of 95-96% sulfuric acid, and 2.5 cc. of 10% aqueous solution of potassium chloride. The salt is substituted for hydrochloric acid because the former evolves less free hydrogen chloride during mixing. Furthermore, potassium chloride is better than sodium chloride since the potassium hydrogen sulfate which is formed in the mixture is much more soluble in strong sulfuric acid than the sodium hydrogen sulfate would be.

When it is particularly desirable to avoid darkening of the tissue it can be accomplished at some expense of color intensity through the use of the following modification of the reagent: 0.05 g. of diphenylamine, 5.0 cc. of 95-96% sulfuric acid, 3.0 cc. of glacial acetic acid, and 2.0 cc. of 12% aqueous solution of potassium chloride.

Summary.

1. Three distinct colors in the diphenylamine reaction are noted. These colors and their intensities could be controlled through variation in the concentration of the sulfuric acid.
2. In the utilization of the diphenylamine reaction as a microchemical test for nitrate nitrogen in plant tissue, it is most important to keep the concentration of the sulfuric acid near 72% in order to obtain the best coloration.
3. Variable temperatures should be avoided throughout any series of tests, since the temperature affects the time for development of maximum coloration.
4. Modifications of the reagent and manner of making the tests are suggested in the accompanying article.

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¹ See Tuemann, "Pflanzenmikrochemie," 1913, p. 82.

A. M. CLOVER.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PARKE DAVIS AND CO.]

PERIODIDES OF CARBONYL COMPOUNDS.

By A. M. CLOVER.

Received March 19, 1920.

Some years¹ ago the writer showed that several different types of organic substances, all possessing the carbonyl group in common, united readily with iodine and potassium iodide to form fairly stable triple addition compounds which crystallized readily, were possessed of a strong metallic lustre and could easily be separated into their components. Pure compounds were prepared with benzophenone, benzoic anhydride and other anhydrides, and it was pointed out that there was evidence of the existence of similar compounds of benzanilide and of methyl oxalate. Careful analyses of several of the pure compounds showed that the formulas of some were relatively simple while those of others were complex; and it was also found that a different combining proportion existed for each of the different bodies which were analyzed. In no case was a perfectly stable substance found, that is, there was always noted at least a slow disengagement of iodine at ordinary temperature and in all cases the iodine of the compounds was readily removed by means of very weak reducing agents.

The results which were obtained in this former investigation naturally brought to mind the well known class of periodides of the alkaloids and other organic bases. Concerning the structure of the periodides derived from these strongly basic substances and the essential function of the nitrogen in their constitution, there can be little doubt. When we compare these with the compounds referred to in the previous paragraph, we find that in the latter case we have generally nonbasic, or at the most, feebly basic substances which may take on a metallic iodide in place of the hydriodic acid of an alkaloidal salt, a further addition of iodine in either case giving rise to periodides, or bodies containing loosely combined iodine. It becomes clear that there must be a fundamental difference between the carbonyl periodides and those derived from strong bases.

In 1891, Scholvien² described a substance which he supposed to be a periodide of acetophenetidine, having the composition $C_{20}H_{22}N_2O_4I_2$. This was patented by Riedel³ and known as *Iodophenin*. Emery⁴ has recently shown that the formula assigned by Scholvien is incorrect and that the latter had a wrong conception of the molecular structure of *Iodophenin*. Emery has proved the correct formula of the body to be $(C_8H_9OC_6H_4NHCOCH_3)_2HI \cdot I_2$ and regards it as an addition compound of

¹ *Am. Chem. J.*, 31, 256 (1904).

² *Pharm. Zentralhalle*, 32, 311 (1891).

³ *D. R. P.* 58409, *Ber.*, 25, 235 Ref. (1892).

⁴ *THIS JOURNAL*, 38, 140 (1916).

the 3 constituents. He considers it a periodide of the hydriodide of acetophenetidine and classes it with the well known basic periodides.

The results of Emery's investigation are not surprising in view of the work of Wheeler and Walden¹ who in 1896 showed that acetanilide combines with iodine and hydriodic acid to form the crystalline addition compounds $(C_6H_5NHCOCH_3)_2HI.I_2$ and $(C_6H_5NHCOCH_3)_2HI.I_4$. These compounds they considered analogous to the periodides of substituted ammonium salts.

Wheeler and Walden naturally made no mention of the acetophenetidine periodide of Scholvien and Riedel for, as has already been stated, the discoverers of this substance, through failure to understand its true constitution, had not properly described it. Shortly afterward, Piutti² in attempting to prepare other periodides similar to the product obtained by Scholvien and Riedel from acetophenetidine, was able to isolate crystalline periodides, which were composed of *p*-ethoxy- or *p*-methoxy-phenylsuccinimide, potassium iodide and iodine and represented as follows: $(C_6H_5O_2NC_6H_4OC_2H_5)_2.KI.I_2$ and $(C_6H_5O_2NC_6H_4OCH_3)_2.KI.I_2$. Extending his experiments beyond the scope originally intended, he isolated a similar crystalline derivative of succinimide to which he assigned the formula $(C_4H_5O_2N)_4.KI.I_4$. This formula has been found by the author to be incorrect, as will appear from the experimental part of this article. However, Piutti undoubtedly isolated a crystalline addition compound between succinimide, potassium iodide and iodine which was more or less contaminated with impurities and with 2 of the derivatives of succinimide he isolated analogous compounds which we may assume to have been pure. The discovery of bodies of this type containing potassium iodide in the molecule was of course not expected by Piutti, and he made no attempt to explain their formation. He concluded, however, that the derivatives of a dibasic acid behaved differently from those of a monobasic acid and was misled into this conclusion by assuming the incorrect formula of Scholvien.

Moore and Thomas,³ in 1914, isolated periodides of benzamide, triple compounds containing as the third constituent sodium iodide, potassium iodide or hydriodic acid. The writer has examined only the potassium iodide compound and as will appear in the experimental part of this article, a different composition must be assigned to it, from the one given by Moore and Thomas. This is a matter of secondary importance, however, and the work of these authors has shown more clearly the relation existing between the periodides of the amide type which had been previously described. They also pointed out that the product described by Curtius⁴ in 1890

¹ *Am. Chem. J.*, 18, 85 (1896).

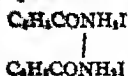
² *Gazz. chim. ital.*, 25, 11, 518 (1895).

³ *This Journal*, 36, 1928 (1914).

⁴ *Ber.*, 23, 3040 (1890).

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and by him represented by the questionable formula



was very likely the benzamide sodium iodide periodide. This substance appears to have been the first of its type to have been isolated.

In 1906, Morgan and Micklethwait¹ described an addition compound of cumarin, hydriodic acid and iodine having the composition $(\text{C}_9\text{H}_6\text{O}_3)_4 \cdot \text{HI} \cdot \text{I}_2$ and considered it comparable to the periodides $(\text{C}_7\text{H}_5\text{O}_2)_2 \cdot \text{HI} \cdot \text{I}_2$ and $(\text{C}_8\text{H}_7\text{O}_2)_2 \cdot \text{HI} \cdot \text{I}_2$, derived from dimethyl pyrone and tetramethyl pyrone respectively by Collie and Steele.² More recently Dox and Gaessler³ have described a periodide of cumarin formed by treating the latter with iodine and potassium iodide and they conclude as the result of their experiments that their product is likely an addition compound of iodine and cumarin. H. Simonis⁴ has found that the compound of Dox and Gaessler contains potassium iodide as one of its chemical constituents and has assigned to it the formula $(\text{C}_9\text{H}_6\text{O}_3)_4 \cdot \text{KI} \cdot \text{I}_2 \cdot \text{H}_2\text{O}$. He has also prepared similar compounds with other metallic iodides and has pointed out that these are only modifications of the periodide which Morgan and Micklethwait obtained with hydriodic acid.

The periodides of cumarin obviously are closely related to those described earlier by the writer. The other periodides which have been considered here are all those of weak bases and have been generally regarded as analogous to the periodides of the ammonium bases and of the alkaloids. The periodides of a ketone, anhydride, ester or a lactone which contain no nitrogen cannot be classed with the above and it is desirable to explain their structure. The authors who have described the periodides of cumarin have overlooked their similarity to those described by the writer. So far as known Simonis attempted no explanation of structure and, as already stated, Morgan and Micklethwait compared their periodide to the pyrone derivatives of Collie and Steele or the periodides of oxonium salts.

Further study of this entire subject has convinced the writer that the power to form periodides is one common to nearly all types of organic substances, containing the carbonyl group. The difficulty in the investigation of the subject is that of obtaining these periodides in pure condition and to do this it is necessary to choose carefully the proper solvent, or mixture of solvents. In solution the compounds are probably broken up to a limited extent into their constituents, any one of which according to its solubility, may separate with, and contaminate the compound. Many of the compounds are very largely broken up by liquids in which they are only sparingly soluble. This difficulty in purification undoubtedly pre-

¹ *J. Chem. Soc.*, 89, 466 (1906).

² *Ibid.*, 77, 1114 (1900).

³ *This Journal*, 39, 114 (1917).

⁴ *C. A.*, 12, 1, 700 (1918); *Ber.*, 50, 1137 (1917).

vents the isolation of a large number of bodies of this class although evidence of their formation may be obtained in several ways: (1) by grinding the constituents together in a mortar or by fusing them together in a test-tube, whereupon a strong metallic lustre will be developed; (2) by bringing the constituents together in a solvent which although not suitable for purification of the compound, will leave a lustrous residue upon evaporation; (3) by grinding in a mortar then spreading in the air and noting whether the iodine is held in combination or readily volatilizes.

Another difficulty is that most carbonyl compounds of relatively low melting point form liquid products with iodine and potassium iodide and of course there is no way of isolating the pure compounds.

Many common organic liquids which, according to their structures, may belong to one of the classes of ketones, anhydrides, esters, etc., will dissolve a mixture of iodine and potassium iodide to a very large extent, whereas the solubility of either of these latter substances, especially that potassium iodide, is usually limited. Ordinary acetone, acetic ester and even olive oil may be given as examples.

A new type of periodide, that of an ester, methyl oxalate, has been isolated and will be described in the experimental part. Crystals of an acetone periodide separate under certain conditions from a solution of iodine and potassium iodide in the solvent. Most of the members of the barbituric acid group readily form pure periodides. With barbituric acid, itself, 2 distinct bodies have been isolated, this result corresponding, in a way, to that of Wheeler and Walden¹ with acetanilide and of Emery¹ with acetophenetidine. A pure triple compound of diethyl-barbituric acid (*Veronal*) has also been studied.

There can be no other conclusion than that in the case of the periodides derived for organic substances containing no nitrogen we have a class quite distinct from the well known one, derived from amine and alkaloidal bases. The evidence is sufficient to conclude that the carbonyl group is the one which is essentially involved in the structure of these substances and the writer proposes that they be designated as *carbonyl periodides*. He would include in this group all derivatives of amides, anilides, etc., which have heretofore been considered as amino or basic derivatives. The reason for this proposed classification is that the acid amides, anilides, etc., are only weak bases and their periodides formed with hydriodic acid or a metallic iodide are very similar in properties to those of the periodides which contain no nitrogen.

The periodides of dimethyl pyrone and tetramethyl pyrone, to which previous reference has been made, were considered by Collie and Steele to be exactly analogous to the periodides of substituted ammonium compounds and the formation of such periodides was considered by these

¹ *Loc. cit.*

authors as very strong evidence of the existence of oxonium salts,¹ compounds of oxygen analogous to ammonium salts. From the facts presented in this article one would be led to consider the bodies of Collie and Steele as carbonyl periodides for the reason that the carbonyl group in general shows such a tendency to form just such compounds and also that no such compounds derived from oxygen differently combined, are known. This matter, along with that of a satisfactory explanation of the structure of the carbonyl periodides, the writer hopes to be able to take up in the near future.

Experimental Part.

Cumarin Potassium Iodide Periodide.

This substance was evidently discovered by Leach,² who employed its formation as a delicate test for cumarin. Dox and Gaessler³ studied its composition and concluded that while potassium iodide was necessary to its formation, the amount found to be present was too small to be considered in assigning a chemical formula. The writer was led to suspect the true nature of the compound at the time of the appearance of Dox and Gaessler's article and the experimental results described here were finished shortly before the publication of the work of Simonis.³ The analytical results of the latter differ somewhat from those obtained by the writer, consequently the same formula is not assigned. Water was used by Simonis as a solvent for purification, while the writer used ether mixed with alcohol or ethyl acetate.

If the ingredients, including powdered potassium iodide, are added to ether, they may be brought into solution by boiling the ether under a reflux condenser. On filtering and cooling the solution, the periodide crystallizes readily. Preliminary analyses of a product made in this way showed approximately its composition, but it was further found that the percentages of iodine and potassium iodide were not close enough to a simple molecular ratio for the product to be considered pure. When the ingredients were first dissolved in a small amount of alcohol, or ethyl acetate, and warm ether was added until the periodide just began to separate, the crystalline product obtained, after filtering and cooling the solution, gave much better analytical results. The periodide is only sparingly soluble in ether and probably suffers considerable dissociation in this solvent. The addition of alcohol or ethyl acetate, in which the substance is very soluble, tends to overcome this difficulty.

Sample I.—Five and three-tenths g. of cumarin, 3.1 g. of iodine and 1.5 g. of potassium iodide were dissolved completely in 10 cc. of alcohol, and warm ether was added gradually until the point of precipitation was

¹ Collie and Tickle, *J. Chem. Soc.*, 73, 710 (1899).

² Leach, "Food Inspection and Analysis," 3rd Ed., p. 362.

³ *Loc. cit.*

reached. The warm solution was filtered and the periodide allowed to separate by cooling the solution. In order to remove the solvent as completely as possible, the crystals were pressed tightly while being filtered, and were closely packed upon a porous plate. The dry crystals were washed by covering them with a small amount of the solvent mixture and again packed tightly on a porous plate. Before analysis, the crystalline mass was well broken up by means of a spatula and placed in a vacuum for one-half hour.

Subs, 0.4208; 9.8 cc 0.1 *N* thiosulfate soln

Subs., 0.4771, KI, 0.0740

Subs, 0.3441, cumarin, 0.1853 g

Subs, 1.7; 0.0037 loss in weight after remaining in a vacuum 2 hrs

Sample II.—The same amounts of the constituents were dissolved in about 20 cc. of ethyl acetate and about 3 volumes of ether was then added. The other details of the operations were the same as in the previous experiment.

Subs, 0.4833, 11.25 cc 0.1 *N* thiosulfate soln

Subs, 0.3789, KI, 0.0584

Subs, 0.3896, cumarin, 0.2075 g

Sample III.—Still another sample was prepared just as the last one, except that a 15% excess of iodine was used. The result was that there was no substantial increase in the percentage of active iodine in the compound.

Subs, 0.5326, 12.75 cc 0.1 *N* thiosulfate soln

Subs, 0.5988, 14.45 cc thiosulfate soln

	Calc for $(C_8H_6O)_2 \cdot (KI)_2 \cdot H_2O$		Found.
	%		%
Active Iodine	29.48	I	29.58
		II	29.54
		III	30.51
Potassium Iodide	15.43	I	15.51
		II	15.41
Cumarin	54.27	I	53.85
		II	53.26

Active iodine was determined by titration with thiosulfate solution. The substance was added to a solution of potassium iodide and the liberation of the iodine was facilitated by warming the solution and by the addition of ethyl acetate to it.

Potassium iodide was determined by heating a sample in an oven at 160° for 2 hours, and weighing the residue. To insure the removal of all of the cumarin, the residue was dissolved in a few drops of water and again heated until it was dry.

Cumarin was determined by dissolving a sample in a small amount of freshly distilled ether with the addition of a couple drops of water; then "molecular" silver was added and the mixture was shaken until the

solution was decolorized. The residue of cumarin obtained from the solution and washings was weighed. The loss of cumarin in a blank experiment was found to be negligible.

Methyl Oxalate Potassium Iodide Periodide.

Two and one-half g. of methyl oxalate was dissolved in 50 cc. of water. Six g. of iodine and 5 g. of potassium iodide were made into a water solution amounting to 20 cc. About $\frac{1}{3}$ of the iodine solution was added to the whole of the former. Crystals of periodide soon appeared and were allowed to settle. The mother liquor was poured off and the crystals were packed tightly upon a porous plate. When nearly dry, they were removed, mixed with a little water and again packed upon a fresh plate. They were finally dried by spreading them in the air for a couple of hours.

SAMPLE I.

Subs., 0.4453, 21.45 cc. 0.1 *N* thiosulfate soln.

Subs., 0.5992, KI, 0.0940

A second crop was obtained from the mother liquor of the previous experiment by again adding about the same amount of the iodine solution.

SAMPLE II.

Subs., 0.3813; 18.50 cc. 0.1 *N* thiosulfate soln.

Subs., 0.5400; KI, 0.0860.

	Calc. for $(C_2H_3O_2)_2.KI.I_2$ %		Found, %
Active Iodine.....	61.23	I	61.17
		II	61.61
Potassium Iodide....	16.00	I	15.69
		II	15.93
Methyl Oxalate (by diff) . .	22.76	I	23.14
		II	22.46

The active iodine was determined by direct titration in water with thiosulfate solution. The potassium iodide was weighed as a residue after evaporation in a dish placed on a steam-bath. It was heated until the weight was constant, a drop of water having been added toward the end of the operation.

This periodide is relatively unstable. During a couple of hours exposure in the air, the loss of iodine is not sufficient to affect the analytical results decidedly, but in a vacuum the loss is rapid. When spread out in a thin layer in the air, the product becomes nearly colorless in 3 days. The crystals are very fine and have a dark bluish-gray lustre. When heated, they begin to melt at about 55° but are not completely fused until 75° is reached. The substance is only sparingly soluble in water but dissolves readily in alcohol, acetone or ether. Crystals may be obtained by adding chloroform to the ether solution.

Periodide of Acetone.

Five g. of iodine and 2.5 g. of potassium iodide were dissolved in about 8 cc. of acetone. On cooling the solution in ice-water, it was converted into a semisolid mass of crystals. The product was quickly removed to a porous plate and as the mother liquor was absorbed, needle-shaped, dark green crystals remained. They were very unstable and, after a couple of hours, a residue of potassium iodide alone remained.

A similar compound of sodium iodide is more conveniently prepared. A saturated solution of iodine in acetone was added to a saturated solution of sodium iodide in the same solvent. The periodide soon separated in very fine needles. These were filtered off, pressed on a porous plate, and washed with acetone in which they are only sparingly soluble. The crystals are not so heavy as those formed with potassium iodide. They are lighter in color and show a golden lustre. When the substance was about free from mother liquor, decomposition began so quickly that an analysis was not considered worth while.

Benzamide Potassium Iodide Periodide.

This substance is especially difficult to purify on account of its dissociation in solution. On the other hand, the dry crystals are very stable. Moore and Thomas¹ purified the compound and also the one derived from sodium iodide, by dissolving it in ether and adding benzene to this solution. They assigned the formulas $(C_6H_5CONH_2)_2 \cdot KI \cdot I_2$ and $(C_6H_5CO \cdot NH_2)_2 \cdot NaI \cdot I_2$ to the salt derivatives. The analytical results of Moore and Thomas are not in good agreement with the theoretical percentages and it seemed desirable to determine the true composition of this representative compound.

It was found that a satisfactory molecular ratio between iodine and potassium iodide could not be obtained by the use of ether and benzene, probably due to the decomposition brought about by the benzene. Better results were obtained when a saturated ethereal solution was cooled in ice-water. The results which were finally found to be acceptable were obtained by bringing the constituents into solution in ether, concentrating this solution as far as possible, then filtering it and cooling it in ice-water.

Sample I.—Two g. of benzamide, 1.2 g. of iodine and 1.0 g. of powdered potassium iodide were gently warmed for a few minutes with about 100 cc. of ether. The solution was filtered and concentrated to about 45 cc. which was again filtered and cooled in ice-water. The crystals are very fine and must be pressed in the funnel to remove mother liquor and finally packed tightly on a porous plate. To wash them, they were covered with a small amount of ether and again packed on a porous plate. When dry, the product was broken up with a spatula and placed in a vacuum for

¹ *Loc. cit.*

a couple of hours. The loss in weight in a vacuum was found to be very slow. The substance melted at 130° , but began to soften a few degrees below this point.

Subs., 0.3176; 0.3131; 8.2 cc. 8.05 cc. 0.1 *N* thiosulfate soln.

Subs., 0.2797; 10.05 cc. 0.1 *N* AgNO₃ soln.

Subs., 0.2726; benzamide, 0.1387.

Sample II.—Two and one-half g. of benzamide, 1.65 g. of iodine and 0.85 g. of powdered potassium iodide were dissolved in about 2.5 cc. of alcohol with careful warming. Fifty cc. of ether was added and the solution was filtered and cooled in ice-water. If much more than the specified amount of alcohol be used, the periodide will fail to separate. This sample was prepared for analysis just as the previous one.

Subs., 0.2994, 7.9 cc. 0.1 *N* thiosulfate soln

Subs., 0.2667, 10.0 cc. 0.1 *N* AgNO₃ soln

Calc. for (C ₇ H ₇ NO) ₂ KI ₂ I ₂		Found	
	%		%
Active Iodine	32.79	I	32.78
		II	32.65
		III	33.51
Potassium Iodide	17.16	I	16.19
		II	17.77
Benzamide.....	50.04		50.88

The active iodine was determined in the same manner as that of the cumarin periodide. To determine the total iodine, water was first added, then a few drops of sulfur dioxide solution sufficient to cause complete decolorization. The iodine in the clear solution was then treated with silver nitrate and ammonium thiocyanate in the usual manner. The potassium iodide was of course calculated from the difference between active iodine and total iodine. The benzamide was weighed directly after dissolving a small sample of periodide in freshly distilled ether and adding a couple of drops of water and sufficient "molecular" silver to decolorize it.

Succinimide Potassium Iodide Periodide.

The compound is readily obtained pure and with a good yield when the constituent parts are dissolved in hot alcohol and the solution is then cooled. On varying the proportion of the components considerably, it has not been possible to affect the composition of the periodide as shown by analysis. When dil. acetic acid is used as a solvent, the yield of periodide is poor and under certain conditions the product is not pure. It seems likely that the product described by Piutti¹ contained free iodine.

The substance has several interesting peculiarities. It is unusually stable and in a stoppered bottle may be preserved indefinitely. It is not perfectly stable, however, and it shows a very slow loss in weight when it is

¹ *Loc. cit.*

spread out well and placed in a vacuum or exposed for a long time in the air. The crystals are light brown in color but lack the metallic lustre which characterizes the other compounds described. This deficiency cannot be due to the relatively small percentage of iodine in the compound, for the analogous body formed from succinic anhydride does show a metallic lustre. The periodide dissolves very readily in water, but it is decomposed by the solvent and a part of its active iodine separates from the solution. It dissolves readily in glacial acetic acid and to a moderate extent in alcohol. The pure substance begins to melt at 141° , but the fusion is not complete until 149° is reached.

Sample I.—Five g. of iodine and 3.2 g. of potassium iodide were added to 6 cc. of water and the solution was filtered to remove a small amount of iodine which remained undissolved. A solution of 4 g. of succinimide in 20 cc. of glacial acetic acid was then added. It was necessary to cool the solution in ice-water and wait for several minutes for the separation of the periodide. The latter was filtered quickly with suction and washed with a few drops of cold acetic acid.

Subs., 0.3702; 9.05 cc. 0.1 *N* thiosulfate soln.

Subs., 0.4044; 15.00 cc. 0.1 *N* AgNO_3 soln.

The active iodine was titrated directly. Total iodine was determined by means of silver nitrate and ammonium thiocyanate after decolorizing the solution with a small amount of sulfurous acid.

Sample II.—Two g. of pulverized potassium iodide, 3.1 g. of iodine and 4.9 g. succinimide were dissolved in about 40 cc. of hot alcohol and the solution filtered. The crystals were washed with alcohol.

Subs., 0.2550; 9.35 cc. 0.1 *N* AgNO_3 soln.

Subs., 0.5150; 12.55 cc. 0.1 *N* thiosulfate soln.

	Calc for $(\text{C}_4\text{H}_5\text{N}(\text{I})_2)_2\text{KI}_2$ %		Found %
Active Iodine.....	31.13	I	31.04
		II	30.94
Potassium Iodide.....	20.34	I	20.99
		II	20.42
Succinimide (by difference)...	48.53	I	47.97
		II	48.64

Succinic Anhydride Potassium Iodide Periodide.

This compound was previously isolated in an impure condition by the writer¹ and a formula assigned which was only in fairly good agreement with the analyses. It was desired to make sure of the correctness of this formula for comparison with the succinimide periodide just described. A pure product has now been obtained by using as a solvent a mixture of chloroform and acetic ether in the proportion of 2 to 1, respectively, by volume.

¹ *Loc. cit.*

5 g. of succinic anhydride, 4 g. of iodine and 3 g. of pulverized potassium iodide were shaken well with a mixture of equal volumes of ethyl acetate and chloroform. An additional volume of chloroform was then added and the solution filtered. Only a part of the anhydride had gone into solution. On cooling the solution in a freezing mixture, crystals separated readily. These were filtered quickly and pressed compactly on a porous plate where they remained until dry. The yield was about 2 g. The mother liquor contained an excess of free iodine and, for this reason, the product was broken up and spread out in the air for 6 hours before analysis. The determinations were made in the same manner as those of the succinimide compound.

Subs., 0.3197; 7.5 cc. 0.1 *N* thiosulfate soln.

Subs., 0.4451; 15.8 cc. 0.1 *N* AgNO₃ soln.

Calc. for (C₄H₄O₃)₂.KI.I.
%

		Found %
Active Iodine	30.97	29.79
Potassium Iodide	20.24	20.00

After exposure to the air overnight, the same sample showed an active iodine content of 29.23%. The compound is unstable compared with that of succinimide. The crystals are very fine and show a decided greenish lustre. The result of the analysis shows clearly the molecular ratio existing between the constituents. This ratio is the same as that found for the succinimide compound.

Periodides of Barbituric Acid.

Barbituric acid and its derivatives readily form periodides which are fairly stable and which generally crystallize from an aqueous solution on the addition of Wagner's reagent. With barbituric acid, itself, it has been possible to isolate in a pure state, 2 different substances whose formation is dependent upon the relative amount of iodine used.

Yellow Crystals, (C₄H₄N₂O₃)₂.(KI)₂.I₂.—Two grams of iodine and 4 g. of potassium iodide were dissolved in about 15 cc. of water and the solution was filtered. This solution was added to one containing 3 g. of anhydrous barbituric acid in 100 cc. of warm water. Crystals appeared at once, the amount of which was increased by cooling the solution in ice-water. They were filtered, washed with a little water and dried on a porous plate. Yield (Sample I), 4.7 g. Another sample was prepared by adding 3 g. of barbituric acid, 2 g. of iodine and 2 g. of potassium iodide to 100 cc. of water and by warming this mixture in a glass stoppered flask until a clear solution resulted. After filtering this solution, the remainder of the operation was carried out as in the previous case. Both samples were exposed to the air a few hours before analysis. In the determination of active iodine it was found best to add an excess of potassium iodide to the solution as iodine shows a tendency to unite with barbituric acid to form a colorless compound.

Sample I.	Subs., 0.4085; 10.85 cc. 0.1 <i>N</i> thiosulfate soln.
	Subs., 0.4462; 16.7 cc. 0.1 <i>N</i> AgNO ₃ soln.
Sample II.	Subs., 0.5804; 15.35 cc. 0.1 <i>N</i> thiosulfate soln.
	Subs., 0.5151; 19.2 cc. 0.1 <i>N</i> AgNO ₃ soln.

	Calc. %		Found. %
Active Iodine	34.08	I	33.73
		II	34.02
Potassium Iodide	17.82	I	18.04
		II	17.39

A 2 g. sample was spread out on a watch-glass and placed in a desiccator over calcium chloride for 3 weeks. It lost 6 mg. in weight. The substance is only sparingly soluble in alcohol and crystallizes from a hot solution on cooling.

Green Crystals, (C₄H₄N₂O₂)₂, (KI)₂, 1₆.—In the preparation of the previous compound the amount of iodine was purposely limited. By using a large excess of the latter, it is possible to isolate green crystals of the composition given above. Although a good yield is obtained, this substance separates only from a solution containing a considerable excess of iodine. The crystals are quickly decomposed by water and as it is impossible to remove the mother liquor completely, the dried product is contaminated with iodine and potassium iodide.

A sample was well packed on a porous plate and allowed to dry. On removing and breaking up the mass of crystals, the presence of uncombined iodine was evident. After exposure of the crystals to the air for 5 hours, the percentage of active iodine in the compound was found to be 52.96; after 24 hours, 52.63; after 3 days, 51.23. From these results the compound appears to be fairly stable. The analyses of this sample and also of a second sample which are used in the calculations were made after the products had been exposed for 24 hours. As would be expected, the percentage of potassium iodide was found to be high.

The samples were prepared as follows: Five g. of iodine and 10 g. of potassium iodide were dissolved in sufficient water to make 12 cc. of solution, which was then filtered through glass wool. One-half g. of anhydrous barbituric acid was dissolved in 20 cc. of hot water. The latter solution was poured quickly into the former and the product was then cooled in ice-water.

Sample I.	Subs., 0.3366; 13.95 cc. 0.1 <i>N</i> thiosulfate soln.
	Subs., 0.3702; 21.75 cc. 0.1 <i>N</i> AgNO ₃ soln.
Sample II.	Subs. 0.4746; 19.40 cc. 0.1 <i>N</i> thiosulfate soln.
	Subs., 0.4671; 27.25 cc. 0.1 <i>N</i> AgNO ₃ soln.

	Calc. %		Found. %
Active Iodine	51.92	I	52.63
		II	51.92
Potassium Iodide	27.15	I	28.73
		II	28.98

It seems remarkable that in these closely related substances we have such a great difference in the number of molecules of barbituric acid contained in the triple compounds.

Diethyl-barbituric Acid Potassium Iodide Periodide.

One g. of diethyl-barbituric acid was dissolved in about 150 cc. of water. One g. of potassium iodide was dissolved in 10 cc. of water and the resulting solution saturated with iodine. On mixing the 2 solutions, the periodide separated at once. The crystals were removed by filtration and transferred to a porous plate. When nearly dry they were washed by moistening them with water, then were again dried thoroughly on a porous plate. Before analysis they were placed in vacuum for $\frac{1}{2}$ hour.

The potassium iodide in Sample I was determined by heating the substance, spread out thinly in a dish, at 150° for 2 hours and weighing the residue after it had been washed well with pure ether. Diethyl-barbituric acid was weighed directly after removing the iodine and potassium iodide. The sample was dissolved in pure ether, a couple of drops of water were added and the solution was shaken with sufficient "molecular" silver to effect complete decolorization. The ether solution was carefully removed and evaporated.

Sample I.	Subs., 0.3180, 12.1 cc. 0.1 <i>N</i> thiosulfate soln.		
	Subs., 0.2358, diethyl-barbituric acid, 0.0847.		
	Subs., 0.2553; potassium iodide, 0.0405		
Sample II.	Subs., 0.4200, 16.05 cc. 0.1 <i>N</i> thiosulfate soln.		
	Subs., 0.4244; diethyl-barbituric acid, 0.1504.		
	Subs., 0.4672; 22.3 cc. 0.1 <i>N</i> AgNO ₃ soln.		
	Calc. for (C ₈ H ₁₀ N ₂ O ₂) ₂ KI I ₂ .		Found
	%		%
Active Iodine. . .	48.75	I	48.29
		II	48.49
Potassium Iodide. . .	15.93	I	15.86
		II	15.80
Diethyl-barbituric acid . .	35.51	I	35.92
		II	35.46

The crystals have a steel-blue lustre and remain unfused when heated to 200° . They dissolve readily in alcohol and acetic acid but only sparingly in water and ether. On varying the proportions of the constituents no other compound could be obtained. The substance is a fairly stable one.

DETROIT, MICH

[CONTRIBUTION FROM TAKAMINE LABORATORY.]

THE PROPERTIES OF A SPECIALLY PREPARED ENZYMIC EXTRACT, POLYZIME, COMPARING ITS STARCH LIQUEFYING POWER WITH MALT DIASTASE.

BY JOKICHI TAKAMINE, JR. AND KOKICHI OSHIMA.

Received March 24, 1920

The aim of this study and article is to compare certain properties of Polyzime, an enzymic extract of *Aspergillus Oryzae* prepared by special processes, with those of standard malt extract.

A. Literature.

"Polyzime," recently invented by Dr. J. Takamine, is an aqueous extract of diastatic enzymes, containing many other enzymes, made by a specially prepared culture of the fungus *Aspergillus Oryzae* on media consisting mainly of wheat bran. As many reports have been published about the enzymes produced by this fungus (generally using Taka-Diastase as sample) a brief abstract will therefore first be given of the important literature directly pertaining to this subject.

J. Wohlgenuth¹ found in a sample of Taka-Diastase amylase, maltase, trypsin, lab. erepsin, lipase and haemolysin. This amylase can resist stronger acid than can pancreatin diastase.

H. C. Sherman and A. P. Tanberg² showed that the amylase of *Aspergillus Oryzae* exerts its maximum activity, both amyloclastic and saccharogenic, in a very slightly acid medium; and as prepared by them it has higher amyloclastic, but lower saccharogenic power than the most active malt amylase preparations yet recorded.

H. C. Sherman, A. W. Thomas and M. E. Baldwin³ reported that the amylase of *Aspergillus Oryzae* showed activity from P_H 2.6 with optimum at P_H 4.8. Pancreatic amylase was active between the limits of P_H 4 and 10 with greatest activity at about 7, the solutions commonly considered neutral showing under similar conditions a P_H value of 5.8. Malt amylase was active between P_H 2.5 and 9 with optimum activity at 4.4 to 4.5. The influence of the concentration of electrolytes, as distinguished from concentration of hydrogen alone, appeared greatest in the case of amylase of pancreatin, and least in the case of the amylase of *Aspergillus Oryzae*.

Experimental.

The results of our numerous experiments on Polyzime preparations and malt extract are as follows.

¹ "Zur Kenntnis der Taka-Diastase," *Biochem. Z.*, 39, 324 (1912).

² "Experiments upon the Amylase of *Aspergillus Oryzae*," *THIS JOURNAL*, 38, 1638 (1916).

³ Influence of hydrogen concentration upon enzymic activity of 3 typical amylases: *THIS JOURNAL*, 61, 231 (1919).

B. General Properties of Polyzyme.

a. Sp. gr., 1.03-1.06.

b. Amylolytic (starch liquefying) power by Wohlgemuth's method: D_{40}^{40} 30 min. = 3,000; D_{24}^{40} hours = 115,000.c. Saccharogenic (starch saccharifying) power by Lintner's method: Lintner's Value (21°) = 43. Lintner's Value (50°) = 150.

d. Chemical Composition:

Water.....	87.5%
Solid Matter.....	12.5
Mineral Matter.....	1.5
Acidity with rosolic acid as indicator:	
10 cc. Polyzyme required 5 cc. 0.1 N acid to neutralize.....	
Total nitrogen.....	0.5
Protein precipitated with Stutzer's reagent.....	0.2%
Reducing sugar as <i>d</i> -glucose.....	2.0%
Amino acid as glyocoll by formaldehyde method.....	1.5
Dextrin.....	1.3

e. Destructive influence of heat.

By placing Polyzyme on a water bath the following decreased percentages of diastatic power after 3 hours were obtained:

Temperature of Water Bath °C.	Decreased Diastatic Power %
15	0
40	0
50	55.0
60	95.0
70	98.0

From the above experiments and many others, it is evidently necessary to preserve Polyzyme at a temperature lower than 40° (104° F.); if the temperature is higher, the diastatic power is decreased proportionately. It is also shown that the optimum temperature for diastase conversion has a destructive influence upon Polyzyme itself during time period of 3 hours or over.

f. Preservation of strength: If Polyzyme is kept in a closed barrel at ordinary temperature it can be preserved for half a year with practically no change of the diastatic power.

C. Amylolytic Power of Polyzyme Compared with Malt Diastase.

I. Method of Experimentation.—There are quite a number of methods for this purpose, such as, for example, Dr. J. Takamine's simple quantitative method of diastatic power determination;¹ William A. Johnson's;² J. Wohlgemuth's;³ S. A. Waksman's.⁴ Among these, the most accurate appears to be that of Wohlgemuth, and to make subsequent data clear, we give here a condensed description of it, as follows.

¹ *J. Soc. Chem. Ind.*, 17, 437 (1898).² "A Proposed Method for Routine Valuation of Diastase Preparation," *THIS JOURNAL*, 30, 301 (1908).³ *Biochem. Z.*, 9, 1 (1908).⁴ *THIS JOURNAL*, 43, 293 (1920).

Wohlgemuth's Method and Scale.—Place in a series of test-tubes diminishing amounts of the enzyme solution to be tested. Introduce into each tube 5 cc. of a 1% solution of soluble starch and place each tube immediately in a bath of ice-water. Transfer the tubes one at a time to a water bath at 40° for 30 minutes (or 24 hours with toluol). At the end of this time transfer again immediately to the ice-water bath to stop the action. Dilute the contents with 20 cc. of water, add one cc. of 0.01 *N* solution of iodine and shake well. One usually obtains colors from blue through violet, red and yellow to colorless, indicative of starch, erythrodextrin, achrodextrin, etc. Take the tube in which the blue or violet has entirely disappeared, giving place to either red or orange-red color as judged by Mulliken's color standard sheet C; note the amount of enzyme solution in this tube and calculate the power of the enzyme as the number of cubic centimeters of one per cent. starch solution which is digested to this stage in a given time by one cc. of enzyme solution.

Thus if 0.2 cc. (or gram) of the substance completely digests 5 cc. of starch solution in 30 minutes at 40°, then one cc. of that solution will be able to digest 250 cc. of one per cent. starch solution; or its power is then stated—

$$D_{30 \text{ min.}}^{40^\circ} = 250 \text{ (Wohlgemuth Scale)}$$

Here the time of reaction is brought into the final expression of diastatic powers that the method may be applied to substances whose power is very slight by allowing them to act a long time.

II. Optimum Reaction of Starch Solution.—We tried to find the best degree of acidity or alkalinity of starch solution for liquefaction with Polyzime. For this purpose we always used Wohlgemuth's method with one per cent. soluble starch solution, but with different concentrations of acid or alkali and at different temperatures. The soluble starch used was a standard preparation and the acidity or alkalinity of the solution was regulated by adding hydrochloric acid or sodium hydroxide, with rosolic acid as indicator. The malt diastase used was one of the

a. 20° and 2 hours $D_{2h.}^{20^\circ} =$		
Reaction of starch soln.	Malt Extract.	Polyzime.
0.0004 <i>M</i> HCl	430	5600
0.0003	660	6000
0.0002	930	6000
0.0001	930	6240
0.0000 (neutral)	930	5000
0.001 <i>M</i> NaOH	730	4200
0.0002	660	3600
0.0003	530	2500

b. 50° and 2 hours. $D_{2h.}^{50^\circ} =$		
Reaction of starch soln.	Malt Extract	Polyzime.
0.0004 <i>M</i> HCl	960	3320
0.0003	1700	16660
0.0002	2800	16660
0.0001	2800	16660
0.0000 (neutral)	2800	16660
0.0001 <i>M</i> NaOH	2800	14000
0.0002	1870	12400
0.0003	1670	11200

best malt extracts on the market with a Lintner's value (saccharifying power) of 380 (50°). The Polyzime used was a standard strength factory product, neutralized with acid. Lintner's value = 150 (50°).

These results indicate that Polyzime and malt diastase show a parallel behavior with changing acidity of a starch solution. Their maximum activities are shown in neutral or very slightly acid solutions. However, Polyzime exhibits a 3 to 5 times greater acidity.

III. Optimum Temperature of Liquefaction.—High temperature accelerates diastatic action, at the same time destroying the diastase itself. Therefore, to determine the optimum temperature, it is necessary to consider the duration of digestion. Wohlgemuth's method was used with one per cent. soluble starch solution, the reaction of which was that of 0.0001 *M* hydrochloric acid, with rosolic acid as indicator. The malt extract and Polyzime were the same as before.

a. 2 Hours and Different Temperature.			$D_{2h}^{10^\circ}$
Temperature. °C.	Malt Extract	Polyzime.	
20	660	4540	
40	2700	15000	
50	2700	15000	
60	1870	6250	
70	833	1000	
80	200	357	

b Different Times and Temperatures.			$D_{10h}^{10^\circ} =$
Duration	Temperature °C.	Malt Extract.	Polyzime.
30 min.....	40	700	3000
	55	1070	4820
	40	2700	16000
2 hours	58	2800	16660
	55	2770	16000
	60	1870	6250
	40	6600	115000
24 hours.....	55	3700	31600

The conclusion to be drawn from the above is that the optimum temperature is about 55° for 30 minutes to 2 hours digestion and 40° for 24 hours. Here also the same relation exists between malt extract and Polyzime diastase.

IV. Comparison of the Amylolytic Powers of Polyzime and Malt Diastase Samples.

The following results were obtained with Polyzime (dry Taka-Koji and Taka-Koji extract) and malt diastases (the best malt flours and extracts) with the Wohlgemuth method and for saccharogenic power tested by Lintner's method:¹

¹ *J. prakt. Chem.*, 34, 385 (1886).

The samples tested (all lately manufactured).

- a. Polyzime "D" (dried Taka-Koji flour, Takamine Laboratory manufactured).
- b. Polyzime (Taka-Koji extract, Takamine Laboratory manufactured).
- c. Malt flour I.
- d. Malt flour II.
- e. Malt flour III.
- f. Malt extract I.
- g. Malt extract II.

	D 40° 30 min	= D 40° 2 h	= D 40° 24 h	= Lintner's value 20°	Lintner's value 50°
a	4700	24000	170000	96	250
b.....	3000	16000	115000	43	150
c.....	1053	4000	10000	156	550
d.....	1000		14000	139	410
e.....	850		15000	128	400
f ...	700	2700	6600	100	380
g ...	400	1000	8632	98	340

Summary.

1. The diastatic power of Polyzime does not decrease at temperatures lower than 40° . Below that temperature it preserves its enzymic activities for more than half a year with practically no change.
2. The optimum reaction of starch solution for liquefaction by Polyzime is neutral or very faintly acid.
3. Polyzime is 3 to 5 times stronger than ordinary malt extract in its amylolastic power as indicated by testing according to Wohlgemuth's method.
4. The optimum temperature of starch liquefaction by Polyzime is 50° for a 30 minute to 2 hours digestion and 40° for 24 hours digestion, although it shows weaker saccharifying power than malt extract tested by Lintner's method.

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THE ESTERIFICATION OF ALPHA AMINO ACIDS.

By H. A. SHONLE AND H. H. MITCHELL.

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In the preparation of amino acids, or in the analysis of proteins by Fischer's ester method, some means of measuring the extent and rate of esterification would be of value. The rate of hydrolysis of a protein can be accurately followed by the Van Slyke amino nitrogen determination (as well as by other excellent methods), but in so far as we are aware, no accurate method has been devised for following quantitatively the subsequent esterification. Such a method would permit a direct determination of the relative merits of the different methods of esterification and

of the best conditions as regards temperature, time, concentration, and other factors under which such methods should be run. In the esterification of amino acid mixtures from proteins and of pure amino acids, much valuable information could be obtained as to the rate and extent of esterification. For example, are the di-amino acids as readily esterified as the monamino acids? Or, does the possibility exist that the diamino acids cannot be esterified by the ordinary procedure? Individual tests on amino acids and comparative tests on proteins containing different amino acids would be of value in clearing up this point.

Three methods have so far been used in following the rate of esterification, or in determining the amount of ester formed from organic acids, namely, (1) the changes in conductivity of the esterifying solution; (2) the actual isolation of the esters formed, and (3) the titration of the un-esterified acidity.

Goldschmidt¹ has shown that, when such a catalyzer as picric acid or trichloroacetic acid is used in an absolute alcoholic solution of the organic acid, the change in conductivity due to the change in the concentration of the water is a satisfactory measure of the velocity of the esterification. While this method would give the velocity of the esterification, the actual amount of the ester formed could be determined only indirectly and with difficulty.

The isolation of the esters formed after a definite period of time, will, in the case of very stable esters, give accurate results. Phelps and Hubbard² used this method very successfully with succinic acid. The succinic ester, after being first freed from traces of acid by treatment with a solution of sodium carbonate, was extracted with ether and distilled under diminished pressure. The accuracy of this method depends upon the stability of the ester and its solubility in organic solvents.

All of the investigations on the esterification of α -amino acids have heretofore depended upon the actual isolation of the α -amino acid ester, yet these esters are quite readily saponified. Investigations, carried out by Abderhalden and Weil,³ show that there is no difference in the yield of glutamic and aspartic acids when their ester hydrochlorides are freed by sodium hydroxide, sodium ethylate, or ammonia. Using Fischer's method of esterification, they isolated and distilled 64.7 to 81.3% of the esters of aspartic acid and 65 to 77.5% of the esters of glutamic acid. The crude esters cannot be weighed as such, since they always contain impurities and, when distillation is the means of purification, there is always an undistillable residue left representing decomposition products of the esters.

Osborne and Jones⁴ modified the regular Fischer method by using the

¹ Goldschmidt, *Elektrochem. Z.*, 13, 4 (1909).

² Phelps and Hubbard, *Am. J. Sci.*, 23, 368 (1907).

³ Abderhalden and Weil, *Z. physiol. Chem.*, 74, 445 (1911).

⁴ Osborne and Jones, *Am. J. Physiol.*, 26, 212 (1910).

Phelps and Hubbard¹ method of esterifying organic acids. They recovered 88.8% of leucine, 85% of glutamic acid and 69.5% of proline from one esterification of weighed amounts of these amino acids. These yields are somewhat higher than those usually secured and this increase is attributed to the superiority of the Phelps and Hubbard method. Levene and Van Slyke² similarly were able to recover 92% of valine in the form of its constant boiling ester, using the Fischer method and liberating the ester hydrochloride with barium hydroxide. Osborne and Jones³ found that 75% of an amino acid mixture is converted into esters at each esterification, calculating on the basis of the esters actually isolated. Many other instances can be cited, all of which show a varying and incomplete esterification.

In all the work of Abderhalden, and Osborne and Jones, on α -amino acids, it must be remembered that the yields of esters obtained are influenced by the incomplete recovery of the esters, due to the unavoidable loss of the esters saponified during the liberation of their hydrochlorides, and due to the inability of the solvent to extract the esters completely from the pasty mass.

In most of the work done in securing the different constants in the esterification of organic acids, the rate of esterification has been followed by titrimetric methods. Goldschmidt,³ Goldschmidt and Sunde,⁴ Kailan,⁵ Thomas and Sudborough,⁶ and many others, have followed this method with satisfactory results. The method itself is quite simple. Definite amounts of alcohol, organic acid and catalyzer are placed in a sealed vessel in a thermostat and aliquot portions are taken out for analysis from time to time. Either 0.2 or 0.1 *N* barium or sodium hydroxide solution is used for the titration with phenolphthalein as an indicator. In cases where the esters are readily saponified, the titration is carried out with ammonium hydroxide and litmus. When hydrochloric acid is used as a catalyzer, the mineral acid acidity can readily be determined from the amount of chlorine present as determined by a Volhard titration.

That this method is best adapted for quantitative work is without question, since it allows the determination, at any period in the process of esterification, of the per cent. of unesterified acidity. In order to apply this method successfully to the esterification of α -amino acids, some means must be taken to overcome the basic influence of the α -amino group, since α -amino acids themselves cannot be determined by titration.

¹ *Loc. cit.*

² Levene and Van Slyke, *J. Biol. Chem.*, 6, 479 (1909).

³ Goldschmidt, *Ber.*, 28, 3218 (1895).

⁴ Goldschmidt and Sunde, *ibid.*, 39, 711 (1906).

⁵ Kailan, *Monatsh.*, 27, 542 (1906).

⁶ Thomas and Sudborough, *Proc. Chem. Soc.*, 27, 314 (1912).

The purpose of the investigation reported in this paper was to modify the titrimetric method in order to adapt it to the determination of the esterification of α -amino acids. The modification used involves the use of the Sørensen formaldehyde titration of amino acids, by which the amino acid acidity is titrated after the destruction of the amino group by condensation with formaldehyde. The technique of the method is described in great detail by Sørensen,¹ both for colorless or colored solutions of amino acids and amino acid mixtures.

Obviously the presence of amino acid esters would not influence the Sørensen titration of the free amino acids, provided that this titration could be conducted in such a way as to avoid any considerable saponification. In obtaining the per cent. of unesterified amino acid acidity at any stage of the process of esterification, samples were withdrawn from the esterifying mixture from time to time and made up to volume. The unesterified amino acids were determined by running a Sørensen titration on an aliquot portion, and deducting the mineral acidity as determined in a second aliquot portion by methods which will be discussed below. The total amino acid acidity was then determined in another aliquot portion. Thus, the per cent. of unesterified amino acid acidity could be calculated from these data by employing the proper correction for volume.

The experimental work of this investigation was conducted mainly on mixtures of amino acids as obtained by hydrolyzing protein, generally casein, with 20% hydrochloric acid, until the Van Slyke amino nitrogen determinations indicated complete hydrolysis. The hydrolyzate was then prepared for esterification in the usual way, after the partial removal of the glutamic acid (usually) and the subsequent removal of the excess hydrochloric acid and water by repeated evaporation with absolute alcohol.

The resulting deeply colored, thick syrup was esterified by the method of Phelps and Hubbard² as applied to amino acid mixtures by Osborne and Jones.² This method of esterification consists in heating the absolute alcoholic solution of the amino acid hydrochlorides and the residual free hydrochloric acid to 100 to 105° in an oil bath, and passing vapors of a boiling 2% solution of alcoholic hydrochloric acid in absolute alcohol through the mixture. The alcoholic hydrochloric acid was made by saturating absolute alcohol with dry hydrogen chloride. Hydrochloric acid was the only catalyzer used. Under these conditions of esterification the water formed during the reaction is presumably removed as fast as formed. At definite intervals during the esterification, 3 to 5 cc. samples of the solution were removed for analysis by means of a pipet.

¹ Sørensen, *Biochem. Z.*, 7, 47, 407 (1907-08).

² *Loc. cit.*

During the course of the investigation many procedures were tested for determining the mineral acidity, for decolorizing the samples, etc., which were afterwards discarded for better ones. A brief description of the experience obtained in the course of the work will illustrate the many difficulties that had to be overcome before a fairly successful method was finally elaborated.

At first the samples removed for analysis were diluted with water and decolorized by the addition of 20 to 30 cc. of aqueous silver nitrate solution (about 0.3 *N*) as recommended by Sørensen. Care was taken that the solution still contained chlorides after this treatment. The silver chloride formed carried down most of the soluble coloring matter. The sample was then made up to a definite volume, usually 100 cc. filtered through a dry filter and aliquot portions submitted to a series of titrations.¹

The total acidity of the sample was determined by a Sørensen titration measuring, (1) the free amino acid acidity, (2) the hydrochloric acid acidity, both that portion originally uncombined and that portion liberated by the condensation of the formaldehyde with the amino groups and with any ammonium chloride present, and (3) the nitric acid acidity added with the silver nitrate.

The total mineral acid acidity present after treatment with formaldehyde was taken as the sum of (1) the total hydrochloric acid acidity as determined by a Volhard chlorine determination, and (2) the total nitric acid acidity as determined from the amount of silver nitrate added during the decolorization of the solution. This determination is based on the assumption that all the mineral acid, free and combined, will be in the uncombined state after treatment with formaldehyde, an assumption which Sørensen found to be correct.

The difference between the value of the Sørensen titration and the determination of the mineral acids by the latter method is a measure of the free amino acid acidity.

The total amino acid acidity was determined by running a Sørensen titration on an aliquot portion of the filtrate which had been completely saponified by boiling with water and dil. hydrochloric acid for 18 hours under a reflux condenser.²

¹ The end-point of the Sørensen titration corresponds to an excess of alkali. Obviously any free alkali is to be avoided when esters are present. Consequently in all the titrations carried on in the presence of esters, the first distinct pink color which corresponds to Sørensen's "second stage" had to be used as the end-point instead of the deep red "third stage." For this same reason it was impossible to add an excess of alkali and titrate back with acid as in the original procedure. The use of this "second stage" gives a value averaging 6 to 8 % below the actual amino acid content of protein hydrolyzates, as can be calculated by applying Sørensen's tables to the analysis of proteins.

² Saponification by means of barium or sodium hydroxide undoubtedly would be

* The mineral acid acidity after saponification could not be determined before saponification, due to the loss of nitric acid during refluxing. It was therefore determined by a titration to litmus as in the ordinary Sørensen procedure. The 2 methods are comparable except for the presence of the dibasic amino acids and ammonium chloride. The titration to litmus would include half the acidity of the former, and none of the hydrochloric acid contained in the latter. The mono-basic amino acids would not be titrated at all, though the hydrochloric acid combined with them would be titrated.

From the total amino acid acidity, as determined by the difference between these 2 titrations on the saponified solution, and the free amino acid acidity as determined on the original sample, the extent of esterification was calculated.

The results obtained from the above methods were not particularly encouraging. The percentage of the unesterified amino acid acidity during the course of 6 to 8 hours esterification exhibited unaccountable fluctuations. It was thought that saponification probably took place during the titration of the aqueous solution of the esters with barium hydroxide. Consequently a series of tests was carried out with amino acid esters obtained from casein. After standing for 18 hours in alcohol of various strengths, the ester solutions were titrated. No saponification could be detected in the 95 and 80% alcoholic solutions. In the 60% alcohol, 64% of the ester was saponified, while in the aqueous solution a 25% saponification resulted. When a Sørensen titration was run on identical amounts of amino acid esters diluted with water, 55, 75 and 95% alcohol, the amount of saponification increased with the increasing per cent. of water. Redistilled alcohol was therefore substituted for water as a diluent. The titrations were carried out with alcoholic silver nitrate and sodium hydroxide.

Several esterifications of the mixtures of amino acids resulting from the hydrolysis of 175 to 200 g. of casein were followed by the method quicker, but there is a danger of the decomposition of the di-amino acids, if present. Also, when tests were run with barium hydroxide as a saponifying agent, a precipitate was always secured which was soluble in hydrochloric acid, and was presumably barium carbonate. Furthermore, glutamic acid is readily converted into pyrrolidone carboxylic acid by boiling in the presence of alkali or by long continued boiling in water (Foreman, *Biochem J.*, 8, 481 (1914).) The esters of glutamic acid (and aspartic acid by analogy) can be saponified by boiling with hydrochloric acid without the intermediate formation of pyrrolidone carboxylic acid. (Abderhalden and Weil, *Z. physiol. Chem.*, 74, 445 (1911).) The other amino acids found in proteins are comparatively readily saponified by boiling with water alone as has been shown by Fischer.

After the acid saponification, a finely divided black precipitate was formed. This was removed by filtering the sample, after it had been made up to a definite volume, through a dry filter. No attempt was made to discover the nature of this precipitate which was negligible in amount.

modified as indicated above. The results are included in Table I. During the time of esterification, 1600 to 1800 cc. of absolute alcoholic hydrochloric acid were passed through the mixture of amino acid hydrochlorides, alcohol and free hydrochloric acid. The bath was kept at a temperature of 110°.

TABLE I.

Expt. 1. Unesterified amino acid acidity, %.	Time in hours	Expt. 2 Unesterified amino acid acidity, %.
63	0 00	64
37	0 50	41
33	1 00	.
.	1 25	36
37	2 00	.
..	2.25	35
33	3.00	..
31	4 00	32
27	5 00	..

The above experiments show that 36% of the amino acid acidity was esterified during the repeated evaporation with absolute alcohol in removing the water. Most of the subsequent esterification occurred during the first hour, and from then on there was a slow and somewhat regular decrease of the unesterified acidity. The slowing up of the esterification was probably due to the difficulty in removing the small amounts of water formed during the esterification by means of alcohol. Considerable trouble was experienced in efficiently decolorizing the samples by means of the silver nitrate method with the result that color formation at the end point of the Sørensen titrations was somewhat masked.

An experiment was carried out on a mixture of amino acids resulting from the hydrolysis of 200 g. of casein, from which the glutamic and aspartic acid had been removed by the method of Foreman.¹ During this procedure an excess of calcium hydroxide was added to the hydrolyzate and the mixture filtered. The filtrate containing the remaining amino acids was light yellow in color, the melanin having been removed by the lime. The calcium was removed and the filtrate was prepared for esterification as usual. About 1500 cc. of alcoholic hydrochloric acid was passed through the mixture of amino acid hydrochlorides. The results are given in Table II.

As it was not necessary to add silver nitrate for decolorization (the mixture remaining clear throughout the run), the mineral acid acidity was entirely due to hydrochloric acid and was determined both before and after saponification by a Volhard chlorine titration. This simplified the procedure and made the determination before and after saponification comparable.

¹ Foreman, *Biochem. J.*, 8, 463 (1914).

TABLE II.

Unesterified amino acid acidity %.	Time in hours.
75.....	0.00
56	0 50
40.....	1.00
47	2.00
43.....	4.00
33	6.00

Since the method of decolorization involving the use of silver nitrate was not found to be efficient, and since it complicated the determination of the mineral acid acidity after saponification, a method which would decolorize the entire solution before esterification without the addition of any inorganic salts or mineral acids other than hydrochloric would be very advantageous. The calcium hydroxide, used in the last experiment, while efficient in decolorizing, was difficult to remove quantitatively.

Denis¹ found that the addition of potassium alum to a colored hydrolyzate made alkaline with sodium carbonate, almost completely decolorized the solution. The soluble coloring matter was carried down with the precipitate of aluminum hydroxide formed. Instead of potassium alum and sodium carbonate, aluminum sulfate and barium hydroxide were used, because they can be quantitatively removed from the solution. The hydrolyzate, after almost all of the hydrochloric acid had been removed by evaporation *in vacuo*, was made slightly alkaline with barium hydroxide. Ten g. of aluminum sulfate was then added for each 100 g. of protein used. The precipitate of aluminum hydroxide, barium sulfate and melanin was filtered off, leaving a clear yellow filtrate which was free from aluminum. To remove the barium quantitatively as the sulfate, it was found necessary to add a slight excess of sulfuric acid and heat the solution to boiling. All the barium was then precipitated as the sulfate, and the excess of acid could be exactly removed by adding barium hydroxide in the hot. The filtrate was then prepared for esterification as usual.

Three esterifications of mixtures of amino acids from, (1) 50 g. of casein, (2) 25 g. of viginin, and (3) 50 g. of gelatin, were followed by the method modified as indicated above. The procedure in each case was practically the same in regard to time, temperature, etc. The temperature of the oil bath was kept sufficiently high (about 120°) so that the temperature of the esterifying mixture was between 100 and 105°. In each case one liter of 2% alcoholic hydrochloric acid was passed through at a constant rate for 8 hours.

¹ Denis, *J. Biol. Chem.*, 8, 431 (1910).

The usual samples were taken off at definite intervals and made up to 50 cc. with redistilled 95% alcohol. A 10 cc. portion was used for a Sørensen titration and a 5 cc. portion for a Volhard chlorine determination. Twenty-five cc. was saponified by boiling with dil. hydrochloric acid for a period of 18 hours under a reflux condenser. The saponified sample was then evaporated on the steam bath to a small volume and made up to the original volume of 25 cc. A 10 cc. portion of this was used for a Sørensen titration, and a 5 cc. portion for a Volhard chlorine determination. By applying the proper volume corrections, the differences between the titrations before saponification will give the free (unesterified) amino acid acidity, while those after saponification will give the total amino acid acidity in terms directly comparable to the first titration. From these 2 values, expressed in cc. of *N* acid, the per cent. of unesterified amino acid acidity can be determined directly. The standard solutions used for the Sørensen titration, however, were 0.2 *N* and those for the Volhard titration were 0.1 *N*. The results of this series are given in Table III in terms of *N* acid.

TABLE III.

Expt. 1, Casein.

Before Saponification.

Time in hours.....	0 00 ^a	0 50	1 50	3 50	5 50	8 00
Total acid.....		2 965	3 336	2 586	4.141	3.434
Mineral acid.....		2 213	2.562	1.995	3.520	2.850
Free amino acid.....		0 752	0 594	0 591	0.621	0.584

After Saponification.

Time in hours.....	0 00 ^a	0 50	1.30	3 50	5.50	8 00
Total acid.....		4.861	5.958	5.073	5.604	5.954
Mineral acid.....		3 385	4.147	3.494	3 832	3.543
Total amino acid.....		1 476	1 811	1 579	1.772	2 411
Unesterified amino acid acidity, %		51	43	38	36	24

Expt. 2, Vignin.

Before Saponification.

Time in hours.....	0 00	0 50	1.50	3.50	5 50	8 00
Total acid.....		2 809	2 311	2 277	3.793	2.155
Mineral acid.....		1 704	1.894	2.794	2.050	1.902
Free amino acid.....		1.105	0.417	0.575	0.227	0.353

After Saponification.

Time in hours.....	0.00	0.50	1.50	3.50	5.50	8.00
Total acid.....		6.877	6.076	5 221	3.046	6.346
Mineral acid.....		5 690	4.702	3.302	1.866	4.002
Total amino acid.....		1.187	1.374	1 919	1 180	2.344
Unesterified amino acid acidity, %	93	30	30	19	16	20

^a The sample taken off at the start gave an impossible result.

Expt. 3, Gelatin.
Before Saponification.

Time in hours.....	0.00	0.50	1.50	3.50	5.50	8.00
Total acid.....	4.780	5.412	4.402	3.036	4.166	3.491
Mineral acid.....	2.860	4.018	3.431	2.474	3.308	3.018
Free amino acid.....	1.920	1.394	0.971	0.562	0.658	0.473
After Saponification.						
Time in hours.....	0.00	0.50	1.50	3.50	5.50	8.00
Total acid.....	8.144	9.125	7.962	4.227	6.350	5.410
Mineral acid.....	5.485	6.182	4.695	2.464	3.798	3.199
Total amino acid.....	2.659	2.943	3.267	1.763	2.552	2.211
Unesterified amino acid acidity, %	72	46	30	32	26	21

No perceptible deepening of the color of the mixture was noticed during the course of esterification. The slightly higher results obtained for the extent of the esterification, as compared with the values obtained in the previous experiments, may be attributed to the slightly higher temperature of the esterifying mixture and the larger proportional amount of alcohol passed through it. From the results shown in Table III, it is evident that the percentage of unesterified amino acid acidity was slowly decreasing at the end of 8 hours. It is probable that the period of esterification used in the work of Osborne and associated (6 to 8 hours) is not sufficiently long to secure maximum results.

The rate of esterification of the casein was somewhat slower than that of the gelatin or viginin, but in the case of the viginin it must be remembered that twice as much alcohol was passed through the esterifying mixture in proportion to the amount of protein used, as in the other cases. At present we are unable to say, because of too little evidence, whether or not qualitative differences in amino acid mixtures will cause definite differences in the rate of their esterification. However, the absence of striking differences in the figures obtained from such different proteins as casein, viginin, and gelatin is significant. The fact that for each protein the extent of esterification at the end of 8 hours is approximately the same is noteworthy, and would indicate that the unesterified amino acid acidity represents an approach to an equilibrium rather than to a definite unesterifiable fraction.

It was found possible to esterify lysine to the extent of 82% in several hours time. Alanine could be esterified to the extent of 96% and glutamic acid 85%. These values are not to be regarded as being maximal in the case of any of the above amino acids. From this we can see that the 3 groups of amino acids present in proteins are esterifiable.

In carrying out the analysis of casein by the Fischer method, several fractions of the ether insoluble residues were secured. These residues very largely consist of the di-amino acids. Upon subjecting these amino acids to the regular procedure for esterification for 20 hours, the following results were secured:

TABLE IV.
Di-amino Acid Fraction.

Time in hours.	Unesterified amino acid acidity. %.
0.00.....	50
1.00.....	45
2.00.....	43
7.00.....	38
11.50.....	27
15.50.....	26
20.50.....	11

A comparison with Tables I, II and III shows that the rate of esterification was slower when the di-amino acids were present in a large concentration.

Several samples of amino acid mixtures from casein were esterified for 20 to 24 hours. In one case it was found possible to reduce the unesterified residue of amino acids to 12%. Unexplainable fluctuations occurred in the percentage of unesterified amino acid acidity during the last 12 hours of esterification. We are planning a series of experiments to determine whether there is a real fluctuation in the actual amount of ester present or whether, due to a possible heterogeneous condition of the syrupy esterification mixture, our method of sampling was at fault. Thus when an amino acid mixture from vegetable albumin was subjected to an esterification for 18 hours, the following results were secured:

TABLE V.

Time in hours	Unesterified amino acid acidity %.
12.0.....	13
15.0.....	9
18.0.....	21

Possibly during the later stages of the esterification as the mixtures become more and more dehydrated, the unesterified amino acids crystallize out of solution and interfere seriously with the sampling.

The accuracy of the above method of determining the extent and the rate of esterification of α -amino acids depends, (1) on the accuracy of the quantitative methods used; (2) on the stability of the amino acid esters during the Sørensen titration; and (3) on the homogeneity of the mixture from which the samples are taken.

The methods used are in themselves accurate for the determination of the ratio of unesterified amino acid to total amino acid content. As shown above, the amino acid esters are stable in 95% alcohol, but they are readily saponified at the concentration of hydroxyl ion required in the Sørensen titration.

The per cent. of amino acid esters saponified during a Sørensen titra-

tion decreases with the increasing concentration of the ester solution. The extent of this is shown in Table VI.

TABLE VI.

Normality of amino acid ester in sample titrated.	Ester saponified during titration. %
0.71.....	1.4
0.25.....	2.4
0.06.....	7.7
0.04.....	8.4
0.02.....	14.6

The amino acid ester concentration in the samples subjected to the Sørensen titration in our procedure varied from 0.1 to 0.2 *N* (see Table III). Accordingly, therefore, a saponification of 5 to 3%, occurred during the titration. Consequently the amount of amino acid acidity titrated is the sum of the unesterified amino acids present in the sample and of that fraction formed by the saponification of the esters during the operation.

However, since the Sørensen titration is discontinued at the "second color stage," the titrations secured are, as shown above, 6 to 8% low. Thus the 3 to 5% of saponification of the esters (in which state 80 to 90% of the total amino acid content of the sample is represented) will be only partially offset by the 6 to 8% undertitration of the amino acids. From these data, the titration of a sample containing 90% of the amino acids as esters will, by the methods used, show an ester content 2 to 3% below the amount actually present. Consequently the reported values of the free amino acid acidity of samples removed near the completion of the esterification are several per cent. high.

Summary and Conclusion.

The rate and extent of esterification of organic acids can be conveniently followed by titrametric methods. In adapting such a method to the esterification of α -amino acids, some means must be used to overcome the basicity of the amino group before the free amino acid acidity can be titrated. The modification employed involves the use of the Sørensen titration of amino acids. The free amino acid acidity in samples withdrawn from the esterification flask, is titrated with the free mineral acid acidity after the destruction of the amino groups and ammonium salts with formaldehyde. The determination of the free and combined hydrochloric acid (the only mineral acid present) is effected by a Volhard chlorine titration. The difference between these titrations represents the free amino acid acidity. The same procedure applied to an aliquot portion of the same sample after saponification with dil. hydrochloric acid, will give the total amino acid acidity. From these 2 results, the per cent. of unesterified amino acid can be readily calculated.

In the case of highly and colored mixtures of amino acids from protein hydrolysis, decolorization was effected by the addition of aluminum sulfate to the hydrolyzate made alkaline with barium hydroxide and subsequent filtration. The barium was removed as the sulfate.

The method has been successfully applied to mixtures of amino acids from casein, vignin, gelatin and vegetable albumin and to mixtures rich in the di-amino acids, as well as to individual amino acids, and shows that in a single esterification as high as 90% of the amino acid acidity may be esterified in the case of amino acid mixtures. Alanine was 96% esterified, lysine 82% and glutamic acid 85%. From the data given a tentative correction of 2 or 3% can be added to the per cent. of amino acid esterified.

From the results obtained in this investigation, it appears that there is no unesterifiable residue of amino acids. The reaction as carried out by the above method is apparently one in which an equilibrium is reached when an appreciable amount of amino acid is still unesterified.

This method will be of value in determining the best conditions under which the esterification of α -amino acids should be run, and in comparing the efficiency of the different methods of esterification.¹

URBANA, ILL.

THE COMBINATION OF FRACTIONATION WITH SPECTROPHOTOMETRY IN PROXIMATE ORGANIC ANALYSIS.²

BY W. R. MATHEWSON.

Received April 7, 1920

In making the chemical examination of various commercial products it is often desirable to estimate with some precision certain colorless substances which are found in quantities of less than a few mg. in the sample available. The spectrophotometric method³ for estimating dyes has the special advantages of being applicable with very small amounts of the coloring matters and requiring no quantitative preliminary purification of them. It has not been largely used for the determination of colorless organic compounds because but few of these substances can be converted easily and completely into colored derivatives by means of reagents that are themselves colorless or widely different in shade. A procedure of somewhat general applicability, however, consists in combining or condensing the substance to be estimated with a suitable compound

¹ An investigation of the cause of the variation of the amount of esters formed during long continued esterification is being planned. The method will also be so modified as to allow the addition (or subtraction) of a correction factor which will include the under-titration as well as the saponification of the amino acid esters.

² Published by permission of the Secretary of Agriculture.

³ For the development of quantitative spectrophotometry, see G. and H. Kruess, "Kolorimetrie und quantitativ Spektralanalyse," Hamburg, 1909.

to form a strongly colored derivative, this being separated then by fractionation with immiscible solvents¹ from other colored substances present in the reaction mixture.

To establish the identity of the colored derivatives several points on their absorption curves may be determined. Most of these substances change in hue or color intensity with acids and alkalis and possess such stability that their dissociation constants as weak acids or bases may be determined by the usual spectrophotometric method.

A few experiments made with test solutions and well known reagents² are described below.³

Sulfanilic Acid.—Ten cc. of the solution to be tested was treated with 1.0 cc. of a 2% solution of picryl chloride in glacial acetic acid, heated to boiling, and allowed to stand 5 minutes. Five cc. of a 1.4% solution of aniline hydrochloride was then added, the mixture again heated to boiling, allowed to stand 5 minutes, cooled, and acidified with 1.6 cc. of 5 *N* hydrochloric acid to bring its acidity to about 0.5 *N*. It was then shaken out successively in 3 funnels with 15 cc. portions of benzene, and the benzene portions washed by shaking with a 15-cc. portion of 0.5 *N* hydrochloric acid, this being passed through the funnels in the same order as the original solution, to which it was finally added. The acid solution was made to a definite volume with 0.5 *N* acid and the light absorption at 435 μ determined.

Five trial solutions treated in this way contained respectively: (a) 0.0030 g. (b) 0.00150 g., and (c) 0.00050 g. dry sulfanilic acid; (d) 0.020 g. pure G. salt (disodium beta-naphthol disulfonate) and 0.020 g. pure sodium-1-naphthol-2-sulfonate; and (e) pure water only. The trinitro-diphenylamine sulfonic acid solution obtained from (a) was diluted to exactly 100 cc. with 0.5 *N* hydrochloric acid and 75 cc. titrated with 0.1 *N* titanium trichloride solution by Knecht and Hilberts' method, adding first an excess of sodium tartrate and a measured amount of Light Green S. F. Yellowish solution to serve as indicator. 2.47 cc. was required to reduce the nitro compound, corresponding to 0.00474 g. of sulfanilic acid in the original solution, or a recovery of 93%. The transmissivity index or extinction coefficient⁴ at 435 μ was found to be 1.07. The solu-

¹ *J. Ind. Eng. Chem.*, 5, 26 (1913).

² Picryl chloride, Turpin, *J. Chem. Soc.*, 59, 714 (1881); Dinitrophenylhydrazine, Purgotti, *Gaz. chim. ital.*, 24, 535 (1899); Borsche, *Ann.*, 357, 180 (1907); diazobenzene sulfonic acid, Ehrlich, *Z. klin. Med.*, 3, 285 (1885).

³ The optical measurements were made with a König-Martens spectrophotometer provided with a heavy brass carrier by means of which the absorption cell could readily be adjusted to allow the full and symmetrical illumination of the slits. One of the compartments of the double cell was filled with the colored solution, the other with the pure solvent (or blank) allowing the transmissivity of the dissolved colored substance to be determined directly. Monochromatic light from a quartz mercury lamp (Cooper-Hewitt, Type Y) was used when the solution under examination showed relatively high absorption for one of the strong mercury lines.

In the calculation it is assumed that within the range of the concentrations employed the specific absorptive power of the colored substance may be considered to be independent of the volume of the solvent. In other words the ratio between the concentrations of 2 solutions is taken to be the same as that between their extinction coefficients or transmissivity indices.

⁴ Bunsen and Roscoe (*Phil. Mag.*, 10, 245 (1857)) defined the extinction coefficient of an absorbing medium as the reciprocal of the thickness of the layer required to reduce the intensity of the incident light to $1/e$ its original value.

tions from (d) and (e) were practically colorless and were discarded. Those from (b) and (c) were diluted to 100 cc. and 50 cc., respectively, and gave indices of 0.35 and 0.25. Assuming proportionality these correspond, respectively, to 0.00155 g. and 0.00055 g. of sulfanilic acid.

Acetone.—A reagent was prepared by dissolving 0.10 g. of 2,4-dinitro-phenyl-hydrazine in 1.0 cc. of warm pyridine and adding 10 cc. of conc. hydrochloric acid. Ten cc. of the aqueous solution to be tested was treated with 5 cc. of the reagent and the mixture allowed to stand 15 minutes in a stoppered bottle. It was then transferred to a separatory funnel with about 7 cc. of 2 *N* hydrochloric acid and shaken out with 3 portions (19 to 20 cc. each) of carbon tetrachloride, these being shaken out successively in a second funnel with a 20-cc. portion of 2 *N* hydrochloric acid. The carbon tetrachloride was then diluted to exactly 60 cc. in a graduated cylinder, and its transmissive index at 435 μ determined and compared with that obtained with a standard carbon tetrachloride solution of pure acetone-dinitrophenyl-hydrazone. Because of slight oxidation or of some impurity in the reagent a very faint coloration was obtained with blanks, being due to a substance similar in its solubilities to the hydrazone.

Ten cc. of a solution containing 0.000508 g. of redistilled commercial c. p. acetone (about 98%, d_4^{25} 0.7862) gave by this procedure a carbon tetrachloride solution having a transmissive index of 0.651. A blank carried through by the same procedure gave 0.053 and a solution of 0.0100 g. of pure acetone-dinitrophenyl-hydrazone in 100 cc. of carbon tetrachloride gave 0.852. 0.000472 g. of acetone was, therefore, recovered from the acid solution.

β -Naphthol.—A diazo solution was prepared by mixing at ordinary temperature 12 cc. of 0.2 *N* sodium sulfanilate, 10 cc. of 0.1 *N* sodium nitrite solution, 20 cc. of *N* hydrochloric acid and sufficient water to make 50 cc. Ten cc. of the aqueous solution to be tested was treated in succession with 5 cc. of the diazo solution, 3 cc. of a 0.1 *N* solution of purified G-salt (disodium beta-naphthol disulfonate), 3 cc. of 5 *N* sodium carbonate solution, and 3 cc. of glacial acetic acid. It was then shaken out in 3 funnels with 25-cc. portions of amyl alcohol and these were washed in the same order with 3 20-cc. portions of *N* acetic acid solution. The amyl alcohol portions were each diluted with 50 cc. of gasoline and the dye completely removed by shaking out with several small portions of water. The aqueous solution thus obtained was treated with 6 cc. of glacial acetic acid and water to bring its volume to 100 cc. A second solution (b) was treated by a similar procedure, but omitting one funnel and one washing portion of acid and making up the sulfobenzene-azo- β -naphthol solution obtained to 25 cc. The transmissive indices were determined at 481 μ –485 μ and compared with that obtained with a standard solution of pure dry Orange II in *N* acetic acid solution. Solution (a) contained 0.00050 g. of β -naphthol; recovered 0.00046 g. Solution (b) contained 0.00050 g.; recovered 0.00043 g.

Summary.

Examples are given of a procedure for the estimation of small amounts of organic compounds which consists in converting them into colored derivatives, these being separated from the excess of the reagents and from any other colored substances present by fractionation with immiscible solvents and finally estimated spectrophotometrically.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS
AND CLARKE UNIVERSITY.]

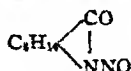
THE DECOMPOSITION OF NITROSO COMPOUNDS. II.

BY WILLIAM A. NOYES AND JAMES A. COSS.

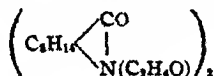
Received April 15, 1920

The work described in this paper was carried out partly at the University of Illinois and partly at Clarke University. It was mostly completed before the closely related work of A. Oppe¹ appeared, but for various reasons publication was delayed. We wish to express our indebtedness to Professor M. A. Rosanoff for the use of the chemical laboratory of Clarke University, in which the latter part of the work was done, and for valuable suggestions made in difficult parts of the investigation.

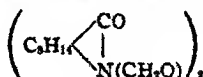
Some years ago Taveau² and one of us found that when the nitroso derivative of the anhydride of amino-lauroic acid,



moistened with ethyl alcohol, is treated with a 10% solution of sodium hydroxide a compound is formed to which the semi-empirical formula,

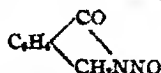


was given. With methyl alcohol a similar compound,



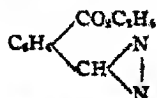
is formed.

A study of the decomposition of nitroso-phthalimidine,



was undertaken in the hope of securing further light on the reaction. It was soon found that when an alcoholic solution of this compound is treated with a small amount of sodium hydroxide the ethyl ester of ethoxy-toluic acid, $\text{C}_2\text{H}_5\text{O}_2\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{OC}_2\text{H}_5$, is formed.

Further study led to the discovery that at a low temperature nitroso-phthalimidine gives diazo-toluic ester,

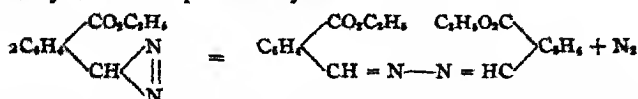


when treated with alcoholic sodium hydroxide. When this red, diazo

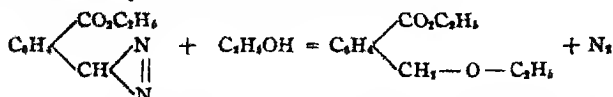
¹ Ber., 46, 1095 (1913).

² Am. Chem. J., 32, 290 (1904).

compound is allowed to stand in an alcoholic solution it changes slowly to the *bis*-hydrazone of phthaldehydic ester:

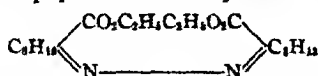


If a solution of the diazo compound in absolute alcohol is boiled, the ethyl ester of ethoxy-toluic acid is formed:

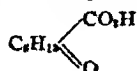


This is, of course, similar to the formation of anisole and other ethers by the action of diazomethane on phenol and other alcohols.

In the light of these results it is evident that the compound referred to at the beginning of this paper is the *bis*-hydrazone of camphononic ester,

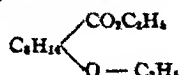


This conclusion was confirmed by hydrolyzing the compound by heating it with hydrochloric acid. This gave camphononic acid,



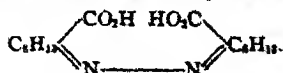
and hydrazine hydrochloride.

The ether ester of hydroxy-lauroic acid,



analogous to the ether ester of hydroxy-toluic acid spoken of above, was also obtained.

The compound spoken of as possibly an azo compound at the close of Taveau's¹ paper was, of course, the *bis*-hydrazone of camphononic acid,



This differs by only 2 hydrogen atoms from the diazo formula suggested and the analytical results for nitrogen and for titration with alkali agree better with the *bis*-hydrazone formula than with the other.

So far as we can discover, no one else has observed the formation of a *bis*-hydrazone from a diazo compound in the manner described in this paper. There seems to be good reason to expect that the reaction may occur in many other similar cases.

¹ *Am. Chem. J.*, 32, 293 (1904).

Experimental Part.

Phthalimide was prepared by a modification of Dunlop's¹ method, using ammonium carbonate in place of urea. Twenty-five g. of phthalic anhydride was mixed with an equal weight of ammonium carbonate and the powdered mixture was heated in a long-necked flask till the whole was in a state of quiet fusion at 300°. After cooling and crystallizing from water, 22 g. of phthalimide was obtained.

Phthalimidine and its Nitroso Derivative, $C_6H_4 \begin{matrix} \diagup CO \\ \diagdown CH_2 \end{matrix} NNO$, were prepared by the method of Graebe,² but the method of Oppé³ is probably better.

Diazo Compound, $C_6H_4 \begin{matrix} \diagup CO_2C_2H_5 \\ \diagdown CH \end{matrix} \begin{matrix} N \\ || \\ N \end{matrix}$.—To 8 g. of nitroso-phthalimidine

dissolved in 30 cc. of ethyl alcohol and cooled with ice and salt, 2 g. of sodium hydroxide dissolved in 20 cc. of alcohol was slowly added. Some nitrogen was evolved and the solution became of a bright red color. After standing in the freezing mixture for an hour large red crystals were formed, these were separated and recrystallized from alcohol. The compound melts at 39°.

Calc. for $C_{10}H_{10}O_2N_2$: C, 63.16, H, 5.26, N, 14.73. Found: C, 62.78, 62.84, H, 5.25, 5.23, N, 15.50, 15.49.

A molecular weight determination by the cryoscopic method gave the following results: 0.2168 g. dissolved in 22.23 g. of benzene gave a depression of 0.253°, and 0.3444 g. gave a depression of 0.416°. These results correspond to a molecular weight of 188 and 182, respectively. Calc. for $C_{10}H_{10}N_2O_2 = 190$.

Bis-hydrazone of Phthaldehydic Acid, $C_6H_4 \begin{matrix} \diagup CO_2C_2H_5 \\ \diagdown CH \end{matrix} - N = N - HC \begin{matrix} \diagup C_2H_5O_2C \\ \diagdown C_2H_5 \end{matrix}$.—

When the diazo compound is allowed to stand in an alcoholic solution, the red color gradually disappears and in 2 or 3 days a yellow compound separates from the solution. When a new solution is gently warmed nitrogen is evolved and the color changes to pale yellow. On cooling and seeding with the yellow crystals, almost the theoretical yield of the bis-hydrazone is obtained. It melts at 145°.

Calc. for $C_{20}H_{20}O_4N_2$: C, 68.18, H, 5.68, N, 7.95. Found: C, 68.20, H, 6.03, N, 8.07.

By the cryoscopic method, 0.1120 g. in 44 g. of benzene gave a de-

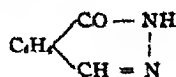
¹ *Am. Chem. J.*, 18, 332 (1896).

² *Ann. Chem.*, 247, 288 (1888).

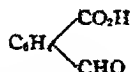
³ *Ber.*, 46, 1099 (1913).

pression of 0.38° , which corresponds to a molecular weight of 324. The molecular weight for the formula $C_{20}H_{20}O_4N_2$ is 352.

Phthalazone and Phthaldehydic Acid.—When the *bis*-hydrazone is heated with conc. hydrochloric acid in a sealed tube at 130° for an hour, phthalazone,



and phthaldehydic acid,

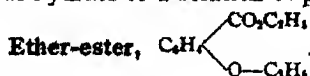


are formed. The phthalazone melted at 183° , and gave, by analysis:

Calc. for $C_{12}H_8N_2O$: C, 68.75; H, 4.11; N, 19.18. Found: C, 65.62, 65.71; H, 4.27, 4.24; N, 19.30, 19.16.

The solution of phthaldehydic acid reduced Fehling's solution and gave a deep red color when warmed with ferric chloride and sulfuric acid.¹

The *bis*-hydrazon, melting at 145° , was also prepared by adding hydrazine hydrate to a solution of phthaldehydic acid.



—When a solution of the red diazo compound in absolute alcohol was boiled nitrogen was rapidly evolved and in half an hour the solution became colorless. The alcohol was distilled off and the oily liquid which remained was distilled under diminished pressure. The major portion came over at 160° , under a pressure of 20 mm. This distillate contained some phthalide, which was removed by washing it with a solution of potassium hydroxide. As it was found difficult to purify the oil, it was saponified by boiling it with an alcoholic solution of potassium hydroxide. After evaporating away the alcohol, the acid was precipitated with hydrochloric acid. It was recrystallized 3 times from hot water, dried and re-esterified by heating it for 4 hours with absolute alcohol containing 5% of hydrochloric acid. The alcohol was distilled off, the residue washed with water, taken up with ether, and the ether distilled. The residue was dried over calcium chloride and distilled under diminished pressure. The clear oily compound had a pleasant, fruity odor.

Calc. for $C_{18}H_{16}O_4$: C, 69.23; H, 6.79. Found: C, 68.60; H, 7.66.

- Molecular weight determinations by the cryoscopic method with benzene as the solvent gave unsatisfactory results, probably due to association. With glacial acetic acid, 0.742 g., in 28 g. of the acid, gave a depression of 0.49° ; 0.4300 g. in 12.89 g. gave a depression of 0.63° . These results correspond to molecular weights of 210 and 205, respectively. The theoretical value is 208. n_D^{25} 1.49556, and d_4^{25} 1.059. This gives a

molar refraction of 57.39 by the formula $\frac{M(n-1)}{(n+2)d}$. Bruhl's values for atomic refractions give the calculated value, 57.46, for the molar refraction.

It is noteworthy that in the method of preparation described the bis-hydrazone as well as the diazo compound is transformed to the ether ester.¹

A portion of the ether ester was decomposed and reduced to *o*-toluic acid by heating it with red phosphorus and hydriodic acid. The latter melted at 104°. 0.0845 g. of the acid required 6.9 cc. of 0.1 *N* sodium hydroxide solution for neutralization. The calculated amount is 6.2 cc. The result is not satisfactory, but it shows that the acid was monobasic.

0.5 g. of the ether acid was oxidized in a sealed tube with nitric acid. The product, after recrystallizing from hot water, melted at 207° and was converted to the anhydride. The latter, after cooling, melted at 128°.

Ethoxy Acid.—This was prepared as described above. It melts at 84.5°.

Calc. for $C_8H_{10}O_3$: C, 66.67; H, 6.72. Found: C, 66.40; H, 6.67.

Subs., 1.1295; 62.94 cc. of 0.1 *N* sodium hydroxide soln. Calc., 62.73.

Derivatives of Amino-lauronic Acid.—When 20 g. of the nitroso derivative of the anhydride of amino-lauronic acid, $C_8H_7 \begin{array}{c} \diagup CO \\ | \\ \diagdown NNO \end{array}$, was added

in small portions to a cooled solution of 2.5 g. of sodium in 75 cc. of absolute alcohol, a bright red color appeared, indicating the formation of the diazo compound. This did not separate, however, as in the case of the derivative of phthalimidine described above. After 3 hours the red color had disappeared and given place to a yellow. The straw-colored solution was diluted with water and extracted with ether. The ethereal solution was washed with water to remove the alcohol, dried with sodium sulfate and the ether distilled. From the residue, by cooling with a freezing mixture, crystals melting at 104° were obtained. These were evidently identical with the compound described by Noyes and Taveau.²

From analogy this compound is evidently the bis-hydrazone of camphonic acid, corresponding to the bis-hydrazone of phthaldehyde acid obtained from phthalimidine. In order to test this interpretation more positively, the compound was hydrolyzed by heating it in a sealed tube

¹ Standinger and Mäckling (*Ber.*, 49, 1973 (1916)) report the formation of the methyl ether ester together with phthalide when the diazo ester is allowed to stand in moist air. They do not seem to have noticed that this is similar to the formation of ethers and esters by the use of diazomethane, and they do not report the bis-hydrazone which we have found. We have noticed the same poisonous, eczema producing quality of the nitroso compound which they found so troublesome.

² *Am. Chem. J.*, 32, 291 (1904).

with 20% hydrochloric acid at 150–160° for 3 hours. This gave camphononic acid, which was identified, after recrystallizing it from water, by its melting point of 230–231°. When mixed with camphononic acid the mixture melted at 232°. In a benzene solution the specific rotation at 22° was 23.2°, while that of a sample of camphononic acid was 23.5°. Potter and Noyes¹ give the rotation as 17.8° at 27.5°.

By evaporating the solution from which the camphononic acid had been separated, hydrazine hydrochloride was obtained. The chlorine in this was determined as silver chloride, the hydrazine by titration with potassium permanganate after adding silver sulfate. The analysis gave:

Subs., 0.0315; AgCl, 0.0880. Subs., 0.0665; N₂H₄, 0.0216.

Calc. for N₂H₄·2HCl: Cl, 67.60; N₂H₄, 30.50. Found: Cl, 69.10; N₂H₄, 32.43.

The results found are not satisfactory, but not enough material was available for us to repeat the analysis.

Ether-ester.—The mother liquors from which the *bis*-hydrazone was crystallized were distilled under a pressure of 3 mm. Most of the material distilled at 113–115°.

Calc. for C₆H₅ $\begin{cases} \text{CO}_2\text{C}_6\text{H}_5 \\ \text{O} - \text{C}_6\text{H}_5 \end{cases}$: C, 68.42; H, 10.52. Found: C, 68.14; H, 10.36.

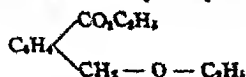
Summary.

1. Phthalimide can be prepared easily and in good yield by heating a mixture of phthalic anhydride with an equal weight of ammonium carbonate.

2. Nitroso-phthalimidine is converted into a diazo compound when a suspension of it in cold absolute alcohol is treated with sodium ethylate. The yield is poor and Oppé's method is probably better.

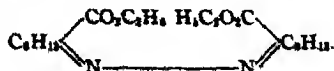
3. When a solution of the red diazo compound in alcohol is warmed gently it is converted to the *bis*-hydrazone of phthaldehydic acid.

4. When a solution of either the diazo compound or of the *bis*-hydrazone in alcohol is boiled, the ether-ester of hydroxy-toluic acid,



is formed.

5. In the light of these results, the compound discovered by Noyes and Taveau was undoubtedly the *bis*-hydrazone of the ester of camphononic acid,

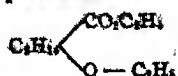


6. In confirmation of this formula this compound was hydrolyzed to camphononic acid and hydrazine.

¹ THIS JOURNAL, 34, 67 (1912).

NOTES.

7. The ether acid of camphonic acid;



is formed when the bis-hydrazone is boiled with alcohol.

URBANA, ILL., AND SIOUX CITY, IA.

NOTES.

Oil of Rubieva Multifida.—A specimen of the essential oil of *Rubieva Multifida*, distilled experimentally by the W. J. Bush Citrus Products Company, at National City, California, from the wild plants growing in the state, was examined.

The oil is light yellow in color and has an odor suggesting anise and terpenes. $d_{25}^{25} = 0.8542$. $[\alpha]_D = +35.75^\circ$ (100 mm. tube).

On the first distillation about 60% comes over at $37-40^\circ$ (under 3 mm. pressure). On repeated refractionation, about 85% of the oil was found to consist of a terpene fraction which, after rectifying over sodium, boils at $169-171^\circ$ (under atmospheric pressure). $d_{20}^{20} = 0.8507$, $[\alpha]_D = +46.4^\circ$ (100 mm. tube).

The terpene fraction polymerizes rapidly on boiling at atmospheric pressure, has an odor resembling that of phellandrene, and yields a nitrosite melting at $103-104^\circ$. Hence it consists largely of β -phellandrene.

From the higher boiling portion of the oil anethole was separated. A resinous residue, probably polymerized phellandrene, was left on distillation.

E. K. NELSON.

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In connection with the writer's recent paper on "The Effect of Surface Oxidation on Some Metallic Catalysts,"¹ his attention has been called to Michael Faraday's work² on the same subject. The investigation of Faraday led to conclusions practically identical with those numbered 1 and 4 in the writer's summary so far as platinum is concerned, namely, that its activity is increased by surface oxidation and is not much affected by reduction. Faraday also studied other phases of the problem, including the effect of the presence of small amounts of various gases. His paper, however, does not deal with the subjects leading to the writer's other conclusions.

FRANK F. RUPERT.

¹ THIS JOURNAL, 42, 402 (1920).

² *Trans. Roy. Soc. (London)*, 124, 35 (1834); "Experimental Researches in Electricity," I, 165.

NEW BOOKS.

Die thermodynamische Berechnung Chemischer Affinitäten von homogenen und heterogenen Gasreaktionen. VON D. IVAR W. CEDERBERG, Privatdozent an der Universität Stockholm. 109 pages. Berlin, 1916. 16 X 24 cm.

The third law of thermodynamics states that the entropy content of solids and liquids becomes zero at the absolute zero of temperature, but makes no statement as to the entropy content of gases. A solution of this latter problem, by further theoretical considerations, is a matter of extreme importance for thermodynamic chemistry. In the book under consideration, using somewhat different language from the above, Cederberg presents what amounts to an attempt to solve the problem of the entropy of gases.

Cederberg believes that Nernst's so-called chemical constant, C , a quantity which is simply related to the entropy of the gas at low temperatures, is equal to the logarithm of the critical pressure, π_0 , for the substance under consideration. He first derives a vapor pressure formula by integrating the Clausius equation

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \quad (1)$$

To carry out the integration he writes for the latent heat of vaporization L , the expression

$$L = L_0 + 2.5RT - 3/4 \epsilon T^{1/4} \quad (2)$$

where L_0 is the heat of vaporization at the absolute zero and ϵ is a constant characteristic of the substance. This formula for L is based on the assumption that all gases have the heat capacity $5/2 R$ at low temperatures and that the heat capacities of both the gaseous and liquid phase increase proportionally to the three-fourths power of the absolute temperature. Substituting (2) in (1) and integrating he obtains

$$\ln p = \frac{-L_0}{RT} + 2.5 \ln T - \frac{\epsilon}{R} T^{1/4} + C \quad (3)$$

where C is Nernst's chemical constant. It is this latter quantity which Cederberg puts equal to the logarithm of the critical pressure π_0 .

Cederberg shows that Equation 3 fits the vapor pressure data reasonably well for a considerable number of substances. C he puts equal to $\ln \pi_0$, and in the majority of cases takes L_0 and ϵ as empirical constants determined by the vapor pressure data. Starting with Equation 3, he also develops methods for calculating heats of reaction, and chemical equilibria in homogeneous and heterogeneous systems.

The reviewer does not believe that Cederberg has presented a completely satisfying solution of the problem he has undertaken. The goal which workers in this field of thermodynamics have set for themselves, ever since the time of Berthelot's unsuccessful attempts, has been to find a

method of calculating chemical equilibria from thermal data alone, without the necessity of making any individual equilibrium measurements. The work of Nernst was an important step in this direction by making such equilibrium predictions possible for condensed phases on the basis of thermal data alone. Nernst's chemical constants, however, still necessitated at least a single equilibrium (*i. e.*, vapor pressure) measurement for gaseous equilibria. Cederberg in equating Nernst's chemical constant to the logarithm of critical pressure has merely specified one particular equilibrium measurement which must be made and hence has not provided a solution of the inherited problem.

Serious attention must also be given to an examination of the strength of the evidence for Cederberg's postulated relationship between chemical constant and critical pressure. In the first place it is obvious that Cederberg's Equation 3 is only approximate. The form in which he takes the Clausius equation (1) is of course itself only approximate, and although his assumption that all gases have the heat capacity $\frac{5}{2}R$ at very low temperatures is to be commended, the assumption that the heat capacities both of solids and liquids increase proportionally to the three-fourths power of the absolute temperature is very far from true. Under the circumstances we cannot hope that his method will give an accurate test of his postulate and must regard it as a still unproven, although a very stimulating suggestion.

Except for these criticisms which may be unduly influenced by the reviewer's own particular point of view, the book is to be recommended as a logical and systematic contribution to thermodynamic chemistry. The text seems free from errors, and the numerous vapor-pressure data and equilibria data which are introduced as examples are in a convenient form for reference.

RICHARD C. TOLMAN.

Éléments de Chimie Générale. By HENRI VAN LAER, Directeur de L'Institut supérieur des Fermentations de Gand Professeur à L'Ecole des Mines et Faculté de Hainaut. Société anonyme, M. Weissenbruch, Bruxelles. 1919 433 pp.

The author has not included a preface in his text, nor given any indication except in the title as to its intended field of usefulness. Apparently, its scope would lie somewhere between the more advanced texts in the subject to which we usually refer pedagogically in the United States as General Chemistry, and an elementary text of Physical Chemistry. As a text-book for elementary instruction in these subjects, the work ought to prove a very welcome addition to the French chemical literature which has not hitherto been so plentifully supplied with texts on physical chemistry as has been the case in English and German. The author's style of treatment is simple, clear and non-mathematical. The text abounds with figures and, while many of them partake of the character of free-hand drawings, they are nevertheless clear and frequently present a cer-

tain originality which is not without its attraction. The text is singularly lacking in experimental data; although it contains some 60 odd figures, there are only one or two brief tables in the entire work. The absence of references to the literature also constitutes a serious detraction.

In keeping strictly to the beaten track followed by the texts of a decade or so ago, the author has, in the opinion of the reviewer, lost an opportunity of presenting much material which should not be omitted from the modern text, even of elementary nature, on General and Physical Chemistry. To dismiss the whole subject of the relation of radioactivity to the elements and their arrangement in the periodic system by a few words appended to the usual statement of the law of the conservation of the elements, to omit all reference to the modern theory of atomic structure, of atomic numbers and of isotopes should not prove a welcome omission to the students of the coming generation. These phenomena are not only of fundamental importance, but are capable of simple and non-mathematical treatment, and have already become of much practical interest.

It is also to be hoped that some time within the coming century all authors can be persuaded by some means to index their works.

S. C. LIND.

Laboratory Directions and Study Questions in Inorganic Chemistry. By ALEXANDER SILVERMAN, Head of the School of Chemistry, University of Pittsburgh, and ADOLBERT W. HARVEY, Instructor in Inorganic Chemistry. Illustrated. D. Van Nostrand Company, New York, 1919. 102 pp. 20 X 26 cm. \$2.00.

The laboratory course presented in this loose-leaf book has been built up during 5 years in the University of Pittsburgh. It contains 55 laboratory assignments and 47 sets of study questions. The titles of the first 18 of the laboratory assignments are quoted to illustrate the character of the course: glass manipulation; physical and chemical change, mixture and compound; purification of substances; oxygen, law of constant proportion; determination of oxygen in air; oxygen and hydrogen, preparation by electrolysis; hydrogen; composition of water, water; water in hydrated barium chloride; osmotic pressure; hydrogen chloride; hydrochloric acid; acid, base, salt; ionization, electrolytes, non-electrolytes; chlorine; acidity of vinegar; chemical equilibrium, speed of reactions; bromine; effect of substances in solution on the freezing and boiling point; etc.

Although it is very difficult to write a set of laboratory experiments which entirely satisfies anyone but the author it is undoubtedly true that the student receives far more benefit from a teacher who has ambition enough to work up an original course than he possibly can from a second-hand course. Not only is this course to be commended on this account, but also because it shows evidence of a great deal of fruitful thought

and labor upon the part of its authors. It is evidently workable, and any student who carries out the experiments outlined will undoubtedly learn a great deal of chemistry.

The following remarks, which the reviewer feels impelled to add, are intended as criticisms of features common to almost all courses in general chemistry, rather than as indicating that the course under review is in any way inferior to others of similar nature.

There are certain ideas emphasized in such courses for the sole reason seemingly that "all of the best people do it." One of these is the distinction between a physical and a chemical change. The writer never sees such a discussion without longing to assume the role of the bold bad student who asks embarrassing questions, and talks back to the instructor; a process, by the way, which ought to be encouraged far more than it is.

Again, we usually find an experiment intended to prove the "law of constant proportion," although one hunts in vain for any clear indication of what it is that is able to vary without disturbing the constancy of the proportion.

Again, students are usually taught to deduce the direction of a shift of equilibrium by the aid of a quantitative expression for the mass law which is unnecessary for the qualitative information sought, and which is not true for the strong electrolytes to which it is frequently applied. Of course, if discipline is good, and the student is trained to accept unquestioningly all that he is told, he may not find out the discrepancy till a year or two later.

If our object is to train men so that they will develop the scientific attitude and understand the scientific method should we not avoid experimental "proofs" which prove nothing, statements of "laws" as rigid which are in fact but approximations? Should we not be eager to give the student a realization of the vast and alluring unexplored regions of chemistry and avoid giving the impression that we have chemistry so thoroughly "doped out" that there is nothing for him to do but to learn such portion of our "dope" as we set before him? Would it not be better to sacrifice a little of the ground to be covered for the sake of developing in the student, capacity for reasoning accurately and clearly, for planning and performing experiments, and for observing accurately what the experiment actually shows, not what the book, in its anxiety to preserve him from error, tells him he ought to see?

The book under review is unusually free from this common error of doing most of the student's thinking for him, although it does seem unfortunate that a formula is deemed necessary to enable the student to calculate percentage composition from the weights of the substances involved.

The above remarks should not be interpreted as indicating that the

book is an inferior one, for the contrary is true, and any teacher of general chemistry would be amply repaid for the time spent in a careful examination of it.

JOEL H. HILDEBRAND.

Inorganic Chemical Synonyms and Other Useful Chemical Data. By ELTON R. DARLING, M.S., Ph.D., in charge of the Industrial Chemistry Department, Newark Technical School, Newark, N. J. D. Van Nostrand Company, New York, 1919. ix. + 100 pp. 11.5 X 18.5 cm. \$1.00 net.

This little book is intended chiefly for the young student of chemistry who finds himself confused by the variety of names given to the more common chemical compounds, but it should also prove to be of value to the business man, who, more or less suddenly, finds that he has to know something about chemicals and their names.

After a short introduction the elements are listed, with symbols, atomic weights, data regarding discovery, and classification into groups. Following this are tables of temperature and specific gravity according to the common systems, with conversion factors. Then come standards of weights and measures in English and metric systems, also with conversion factors.

In the next 70 pages are listed chemical synonyms for certain compounds of the following elements: aluminum, antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, silver, sodium and zinc; and in the final 20 pages are given some 75 miscellaneous terms, a list of names of certain hydrogen compounds, and a cross index listing about 400 synonyms.

The book is not intended to be complete, and indeed it is very far from complete. Furthermore, the basis for the selection of terms and other information given is a little difficult to understand. The reader undoubtedly will be much interested in learning that bismuth oxynitrate has 12 synonyms, that "spanish white" may be either this substance or calcium carbonate, and that "oil pulp" and "red liquor" are both synonyms for aluminum acetate. One wonders, however, why "kali preparatum" and "yellow wash" are included, and Moore's salt, or tin crystals, or argols omitted; or why so many Latin synonyms are given, and so few compounds of each element and so few elements. Again, in the section on the discovery of the elements it is disappointing to find that nothing is said about tin and sulfur, both exceedingly important elements, and that gold and native copper are not mentioned in the list headed, "Occurrence of the Metals in Nature."

The typography and the makeup of the book are satisfactory, but it is unfortunate that the proof-reading has been done so carelessly. There is scarcely a page without one or more very evident errors, which occa-

tionally may lead to serious misinformation, as on p. 88, for example, where the synonym for "diasotizing (*sic*) salts" is given as sodium nitrate; or as on p. 54, where it is stated that ferric iron has a valence of 4; or as on p. 93, where phosphate of lime is referred to calcium sulfate. A new edition, however, should allow all such errors to be corrected, and, furthermore, should make possible a revision of many hastily written sentences, as on p. 46. "The use of lime in the preparation of mortar for building belongs to the pages of unknown history;" or as on p. 31, "Davy * * * tried to purify the metal * * * " (instead of *prepare*); or as on p. 25, "The litre is equal to a cubic decimeter." There is also some question as to the justification for the author's spelling "phosforus," since both the ph and f are derived from the same Greek letter, ϕ . The table of atomic weights should, of course, be dated.

The book is a sincere attempt to make the way of the student of chemistry a little easier, and as such deserves commendation. The need for summaries, monographs—books which shall gather into small space much scattered information,—is increasing geometrically with the growth of science. This one by Dr. Darling should be welcomed.

WILLIS A. BOUGHTON.

Plant Products and Chemical Fertilizers. By S. HOARE COLLINS, Lecturer and Adviser in Agricultural Chemistry, Armstrong College, Newcastle-on-Tyne (University of Durham). D. Van Nostrand Company, New York, 1919. xvi + 236 pp.

This is one of a series of volumes on industrial chemistry edited by Samuel Rideal, of University College, London. In this the editor and his associates propose to offer "a comprehensive survey of the chemical industries." The editor points out in his general preface, "The rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world * * * Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention * * * Present tendencies and possible future developments will have attention and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries * * * As far as this country is concerned, it is believed that the general scheme of this series of hand books is unique, and it is confidently hoped that it will supply mental munitions for the coming industrial war."

The present volume is divided into 4 parts, dealing respectively, with,

Fertilizers, Soils, Crops and the Production of Meat. The subdivisions of the first part are of Nitrogen Groups of Fertilizers; The Phosphorus Group of Fertilizers, Potassium Group of Fertilizers, Mixed Fertilizers. The second part contains sections on, Soils and Their Properties; Special Soil Improvers; Soil Reclamation. The third part contains 6 sections, namely, Photosynthesis; The Carbohydrates Produced in Crops; The Oil Bearing Plants; The Nitrogen Compounds in Plants; Miscellaneous Plant Products; Produce Variability. The subdivisions in Part 4 are entitled, Manuring for Meat; The Foods Fed to Beasts; Calorific Value of Foods; Dairy Products; Future Developments.

While the discussion of each of the numerous topics included in the book is of necessity brief, the author shows a splendid grasp of his subject. His statements are clear, concise, and very much to the point. He tells us, for instance, "It does not always pay to produce maximum crops, and hence some lands are said to be so fertile as not to need fertilizers. The present war is teaching us that too much reliance may be put upon the economic aspect of food production; that the interests of the nation are not identical with those of the producer." (p. 2.) A few additional sentences may be quoted to show the author's effectiveness of statement; "No soil is perfect; no soil quite hopeless; much can be done to improve the bad, and much can be left undone to injure the good." (p. 3) "The power of fertilizer to act quickly or slowly is a very important property." (p. 4) "In considering the actions of fertilizers on the plant and on the soil it is always important to remember that in no sense is such a series of actions a static matter." (p. 5) "In the vicinity of large towns the sulfur thrown into the atmosphere by the combustion of coal comes down with the rain, washes into the soil, combines with lime, and produces calcium sulfate." (p. 75) "Both maize and rice lend themselves to the possibility of producing starch by the dry methods of grinding and blowing by currents of air, but starch is chiefly made by one of the wet methods." (p. 121).

Some of the author's statements are subject to correction. For example, he claims that solutions of superphosphates or ammonium sulfate "would be absolutely injurious to the plant" when grown in water culture (p. 13). This will depend, of course, on the degree of dilution. In speaking of the impurities in nitrate of soda he fails to mention borates (p. 19). Calcium cyanamide is not "a slow acting manure" as is claimed by the author (p. 22). The author is hardly justified in stating "The really most important member of the group of potassium fertilizers is, however, farmyard manure." (p. 39). It is not true that "A low quality of lime * * * is of no use for agricultural purposes" (p. 86). All told, however, the author has succeeded in producing a very readable and very useful book.

J. G. LIPMAN.

Qualitative Chemical Analysis. By W. W. SCOTT. Third Edition, revised and enlarged. 330 pp. Cloth. 13 X 19 cm. D. Van Nostrand Co., New York, 1928. \$2.50.

The third edition of this text-book on qualitative analysis varies but little in appearance, plan and scope from the previous edition. Another section has been added, however, which is devoted to a discussion of the reaction properties of a number of the less common elements which, as the author says, "are important on account of their technical use." The contents of the book are divided into 6 parts: Part I, Introduction and the Theory of Analytical Reactions, 25 pp.; Part II, Reactions and Separations of Cations, 128 pp.; Part III, The Anions, 57 pp.; Part IV, Systematic Analysis of a Substance, 29 pp.; Part V, Tables of Reactions of the Metals, 53 pp. Part VI, The Less Common Elements, 30 pp.; Index.

The book contains an unusual amount of data of value to an individual engaged in routine analytical work and will commend itself, therefore (particularly), to those employed in commercial laboratories.

It is the opinion of the reviewer that the majority of teachers would approve of a rather fuller discussion of "oxidation and reduction" and the presentation of the method for formulating these reactions from the standpoint of the ionic hypothesis. The same may be said with reference to the author's treatment of the solubility product. The choice of the mathematical expression of the latter rather than the one involving its expression in terms of concentration seems somewhat unfortunate. Likewise, it is to be regretted that the author makes no reference to the limitations of the statement with reference to concentrated solutions and abnormal electrolytes. The pedagogical usefulness of the book would be increased if the author should see fit to incorporate restatements of these principles and a discussion of their applications to analytical procedures in the "Notes" relating to group separations, etc.

The properties of each base-forming and acid-forming substance are described before taking up the methods for their grouping and separation. However, only those reactions which are to be employed by the student in following the methods outlined for their identification are presented in the general scheme. A more extended list of reactions is presented in Part V. The methods described for the grouping and separation of the cations and anions are similar to those found in most text-books of qualitative analysis. However, many chemists would probably object to the author's inclusion of molybdenum, tantalum, tellurium and tungsten in the hydrochloric acid group. No reference is made to the well-known perchlorate method for the separation of sodium and potassium. There is an abundance of notes and precautions distributed throughout the book. The mechanical features of the text-book are good and but few misprints were noted by the reviewer. On p. 14, C_2H_4 should be C_2O_4 ; and on p. 330, in the preparation of stannous chloride, NH_4Cl should be HCl .

RICHARD EDWIN LEE.

